Inês Alexandra Barros Serra Duarte

Licenciada em Ciências de Engenharia do Ambiente

The main leachate emissions of uncontrolled landfills

Dissertação para obtenção do Grau de Mestre em Engenharia do Ambiente, Perfil de Engenharia Sanitária

Orientador: Prof. Doutora Ana Isabel Espinha Silveira, Professor Auxiliar, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa

Co-orientador: Doutor Engenheiro Roberto Raga, Investigador e Professor com Agregação, Università degli Studi di Padova

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FACULDADE DE CIÊNCIAS E TECNOLOGIA
UNIVERSIDADE NOVA DE LISBOA

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"(…) the real way to get happiness is by giving out happiness to other people. Try and leave this world a little better than you found it (…)"

"(…) o melhor meio para alcançar a felicidade é contribuir para a felicidade dos outros. Procurai deixar o mundo um pouco melhor de que o encontrastes (…)"

Robert Baden-Powell

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Abstract

One of the biggest current problems is the proper management of solid waste and other waste streams. All types of waste have a potential pollutant affecting soil resources and water resources, mainly in landfills that may not have adequate protection measures and do not know the waste placed in them.

Through the study on laboratory scale it is possible to check which potential emissions to the level of leachates of uncontrolled landfills. The leachates can be compared. It is possible to say which ones have more heavy metals and organic fraction emissions.

This study analyzed samples of leachate from two landfill waste in North-East Italy, near Verona, two old uncontrolled landfills. The leachate samples come from the simulation of biological reactors, operated in aerobic and anaerobic condition. The leachates were characterized in terms of pH, heavy metals such as Cd, Cr, Cu, Fe, Mn, Ni Pb, Zn, As and Hg and organic fraction (TOC, TKN and NO_3).

The heavy metal and organic fraction concentrations were found low in order of micrograms, and in the organic fraction in order of milligrams, per litre of leachates. In general, the concentrations in the anaerobic bioreactors were higher than in the aerobic bioreactors.

The study showed that pH is a very important factor regarding the mobility of the metals in the leachate. The quality of the leachates in study have little potential for water pollution since they exhibit basic pH values (around 8), even if the residues are saturated, that is, the ability of field reached.

Keywords: Landfill, uncontrolled, leachate, heavy metals, bioreactors.

Resumo

Um dos maiores problemas actuais é a correcta gestão dos resíduos sólidos urbanos e de outros fluxos de resíduos. Todos os tipos de resíduos têm um potencial poluente que afectam os recursos pedológicos e os recursos hídricos, principalmente em aterros que não tenham adequada protecção e não se conhecem os resíduos neles colocados.

Através do estudo em escala laboratorial é possível verificar quais as potenciais emissões ao nível de lixiviados de aterros não controlados. É possível comparar também as emissões de metais pesados e fracção orgânica nos diversos lixiviados.

Neste trabalho foram analisadas amostras de lixiviados de resíduos de dois aterros no Nordeste de Itália, perto de Verona, dois antigos aterros não controlados. As amostras de lixiviados provêm da simulação de bioreactores, operados em condição de anaerobiose e aerobiose. Os lixiviados foram caracterizados em termos de pH, metais pesados como Cd, Cr, Cu, Fe, Mn, Ni Pb, Zn, As e Hg e fracção orgânica (COT, TKN e NO_3).

As concentrações de metais pesados encontradas foram baixas, na ordem de microgramas do metal pesado, e da fracção orgânica na ordem das miligramas, em estudo por litros de lixiviado. Em geral, as concentrações nos bioreactores anaeróbios foram menores de que nos bioreactores aeróbios.

O estudo mostrou que o pH é um factor muito importante no que diz respeito a mobilidade dos metais nos lixiviados. A qualidade dos lixiviados em estudo tem um potencial pouco poluente para os recursos hídricos visto que apresentam valores de pH básico (8), mesmo que os resíduos se encontrem saturados, isto é, com a capacidade de campo atingida.

Palavras-chave: Aterro, não controlado, lixiviado, metais pesados, bioreactores.

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Abbreviation Index

Al – Aluminum

AOX – Halogenated organic compounds

As – Arsenic

BTEX – Group of compounds formed by hydrocarbons

BOD – Biochemical Oxygen Demand

C – Concentration of the parameter

Ca – Calcium

Cd – Cadmium

C&R – Construction and demolition debris

Cl – Chlorine

CH_4 – methane

Cr – Chromium

COD – Chemical Oxygen Demand

Cu – Copper

DM – Dry Matter

EETI – Eurofins Environment Testing Italy

Fe - Iron

FWinput – Volume of the fresh water added after collected sample

Hg – Mercury

ICP-OES – Inductively Coupled Plasma Optical Emission Spectrometry

IR_4 – Respiration index

K - Potassium

LISA – Laboratorio di Ingegneria Sanitaria Ambientale

LSR – Landfill simulation reactors

L/S ratio – Water (in litres) passing through a given waste mass (in kg dry matter of waste)

Mg - Magnesium

Mn - Manganese

MSW – Municipal Solid Waste

MSWI – Municipal Solid Waste and Industrial Waste

Na – Sodium

Ni – Nickel

NH_3 - Ammonia

$N\text{-}NH_4$ - Ammonium

$N\text{-}NO_2$ - Nitrogen Dioxide

$N\text{-}NO_3$ – Nitrate

P - Phosphorus

Pb – Lead

SCmix – Mixture of five samples collected at "Servizi Costieri S.r.l" landfill

SCmixA – SCmix in anaerobic conditions

SCmixB – SCmix in aerobic conditions

SC1 – Sample collected on drilling number 1 at "Servizi Costieri S.r.l" landfill

SC2 – Sample collected on drilling number 2 at "Servizi Costieri S.r.l" landfill

SC3 – Sample collected on drilling number 3 at "Servizi Costieri S.r.l" landfill

SC4 – Sample collected on drilling number 4 at "Servizi Costieri S.r.l" landfill

SC5 – Sample collected on drilling number 5 at "Servizi Costieri S.r.l" landfill

SO_4 – Sulphate

TOC – Total Organic Carbon

TKN – Total Kjeldahl Nitrogen

TotalFW – Total volume of Fresh Water addicted on the bioreactor

TS – Total Solids

UV-VIS – Ultraviolet–Visible Spectroscopy

V ext. – Volume of leachate extracted

Vmix – Mixture of five samples collected "Noè-Tebaldi" landfill

VmixA – Vmix in anaerobic conditions

VmixB – Vmix in aerobic conditions

V1 – Sample collected on drilling number 1 at "Noè-Tebaldi" landfill

V2 – Sample collected on drilling number 2 at "Noè-Tebaldi" landfill

V2A – V2 in anaerobic conditions

V2B – V2 in aerobic conditions

V3 – Sample collected on drilling number 3 at "Noè-Tebaldi" landfill

V4 – Sample collected on drilling number 4 at "Noè-Tebaldi" landfill

V5 – Sample collected on drilling number 5 at "Noè-Tebaldi" landfill

WHC – Water Hold Capacity

Zn - Zinc

1 Introduction

1.1 Framework

The problematic of waste has to have greater importance. This problematic is being associated to the potential negative impacts on the environment.

The primitive societies do not have problem with the disposal waste. The population was small and the assimilation of wastes was large for the amount of land available (Carra and Cossu, 1990). The waste production never was a problem since it was deposit away from the population. The waste was deposit indiscriminately and without concern for the separation of the different types of waste.

However, the waste was a problem with the appearance of areas with large population as tribes, villages, and communities (Carra and Cossu, 1990; Tchobanoglous *et al.*, 1993). For example, in Athens, the first "municipal landfill" (dump/ uncontrolled landfill) was created 500 b.C. and de waste was deposited there one mille of the city. The accumulation of wastes became a consequence of life (Tchobanoglous *et al.*, 1993).

The next centuries were characterized by throwing wastes in to vacant land unpaved, streets and roads (Tchobanoglous *et al.*, 1993). This practise of throw the waste out door was came customary and lasted until the mid-twentieth century. This type of practices led to of the most deadly epidemic plague eve, the Black Death, which was responsible to kill half of the Europe population in fourteenth-century (Tchobanoglous *et al.*, 1993). The Industrial Revolution was a period that the solid waste disposal problems increase due to industrial waste includes toxic elements.

Over the centuries, the types of the waste were different. The composition and the production of the waste depend of the country, city, and culture. These also depend on the society and its economical development. In general, economically developed societies are more polluting than the developing societies.

It is possible to see that exist a relationship between public health and solid waste. The United States Public Health Service has publishes a study describing the relationship between twenty-two human diseases and improper solid waste (Tchobanoglous *et al.*, 1993).

The open uncontrolled landfill were the main problem due proliferation of many disease vectors such as rats and flies (Tchobanoglous *et al.*, 1993). Uncontrolled landfills have other problems as the ecological ones associated to improper management, being the most importants problems the water and air pollution.

Uncontrolled landfills, such as sanitary landfills, can be considered a biochemical reactor where the inputs are waste, storm water and energy, and outputs biogas and leachate resulting from the degradation of the waste and precipitation (Levy and Cabeças, 2006).

The leachate is an inevitable consequence of waste disposal, and water balance is a result of disposal sites and the percolation of water into the waste mass that draws and drags many dissolved and/or suspended materials (Tchobanogluos *et al.*, 1993; Qasin and Chiang, 1994). The leachate produced from uncontrolled landfill and poorly engineering landfills may contain toxic elements, such as copper, arsenic, uranium (Tchobanoglous *et al.*, 1993), cadmium, chromium, lead, etc., and contaminate water supplies with unwanted salts (calcium and magnesium) that can contaminate surface water and groundwater above and around the mining area (Tchobanoglous *et al.*, 1993).

Therefore ecological imbalances have occurred where the nature assimilative capacity has been exceeded, even nature has the capacity to dilute, disperse, degrade and absorb, reducing the impact of unwanted residues in the waterways (Tchobanoglous *et al.*, 1993).

Even after the uncontrolled landfills closed, ecological problems may persist, if the methods used were not the correct ones. The closure of uncontrolled landfills should contemplate conveniently studied, implemented and monitored technical solutions. A contrary situation, the associated risks of uncontrolled landfills translate health and

environmental problems such as those negative impacts listed below (Levy and Cabeças, 2006):

- Human health risk
- Fauna and flora damage
- Quality degradation of surface water and groundwater
- Quality degradation of air
- Quality degradation of soil
- Degradation of the local landscape

1.2 Objectives

Conscious of the problem of pollution by leachate in general and from uncontrolled landfills and open dumps in particularly, the thesis is framed in the potential risk of pollution of the environment around of uncontrolled disposal sites.

In waste disposal sites which were not controlled since the first disposal, the leachate collection was not done and, it is probably, pollution source for groundwater and soil under the disposal site and for surface water next to de discharge of waste.

The main goals of the thesis highlight the following:

1. Study of the leachate potential pollution (main emissions) of two uncontrolled landfills, with focus on heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn, As and Hg) and organic fraction (TOC, TKN and NO_3);

2. Compare the compounds levels in the leachate from simulated aerobic and anaerobic bioreactors;

3. Determine the remaining potential pollution using a liquid to solid ratio (L/S ratio).

1.3 General methodology

The first phase consisted of a desk research in books, technical reports, dissertations, research papers and legislation, available either in digital form or in physical format. It allowed for greater knowledge about potential pollution at landfills, uncontrolled landfills and dumps, including the existing legislation and studies already undertaken. It allowed greater insight into leachate and its negative environmental impacts and socially. It was possible to understand what the best parameters to assess qualitatively and quantitatively the leachate and which metals more reviews and relevant in the study of potential leachate pollution.

The second phase of this work was based on testing of leachate samples. The samples were produced by the leach of residues from holes of two uncontrolled landfills. The simulation was performed under conditions of saturation, flooding or waste in the water level rise scenario. To compare tests were carried out parallel subjecting various samples of waste aerobic and anaerobic conditions. Thus, made the determination of pH, conductivity and heavy metals present in their leachate.

In a third phase a new documentary research in books, technical reports, dissertations, research papers and legislation to complement the theoretical basis of the work.

1.4 Thesis Overview

This dissertation is organized into six chapters.

The first chapter consists of a framework approach to the dissertation topic. It also exposed the main objectives of this work, as well as the methodology for its implementation and structure of the dissertation.

The second chapter consists of a compilation resulting from the literature review, concerning legislation in Europe, Italy and Portugal; definition and characterization of dumps, uncontrolled landfills and landfills; parameters characterizing the age of

landfills; definition and characterization of leachate, L/S ratio, organic matter, and heavy metals and their mobilization.

The third chapter includes a brief description of case studies related to the topic addressed in this paper. The studies covered are study in which laboratory leaching tests were performed in different conditions of aeration and also studies done with samples of waste from different waste streams.

The fourth chapter describes the methodology used in the practical component, including waste samples, reactor preparation, selection of parameters for analysis, work planning, methods of analysis of the leachate and processing data.

The fifth chapter consists of the analysis and discussion of the results of experimental component, namely the leaching tests carried out in different conditions of aeration at two different samples of in landfills not controlled laboratory environment. It still discussed results of analyzes of the leachate produced, especially for pH, heavy metals and organic fraction as a function of L/S ratio.

The sixth chapter is a concluding summary about the work done, which includes the main results. It also indicated some proposals for future work.

2 Literature Review

2.1 Legal framework

Throughout the humanity' evolution, environmental problems resulting from the accumulation of disordered residues were increasing. Thus it was necessary, by governments, to create legislation to control the production of waste and resource depletion.

Europe was producing legislation addressing the issue of waste and its deposition by directives mandatory adaptation, enriched the national legislation of its Member States.

2.1.1 Legal framework in Europe

Since 1970's that European Union tries to minimize the damage in the environment, either in ground or in the hydrologic resource.

In 1971, European Parliament published a recommendation that suggested the waste reduction and reutilization. The recommendation was supported by the First Communitary Action Program for Environment.

In 1975, the first Directive regarding waste was published. According the Council Directive 75/442/EEC of 15 July 1975, concerning waste, refers that it should be applied an effective and consistent regulations on waste disposal which neither obstruct infra-community trade nor affect conditions of competition should be applied to movable property which the owner disposes of or is requires to dispose of under the provisions of national law in force. The Directive 75/442/EEC of 15 July 1975, refers is essential objective of all provisions relating to waste disposal must be the protection of human health and the environment against harmful effects caused by the collection, transport, treatment, storage and tipping of waste.

In 1987, the European Parliament made a resolution to warn the extent and severity of the problems, contamination of soil, water and air, resulting from improper waste management. The following year the Commission adopted the regulation document "Strategy for EEC Waste Management", which called for direct reduction of waste flows, the best possible treatment and ultimate destination, transboundary movements reduction and civil liability.

In the last years of the decade of the 80s, and during the 90s, the European Union published several directives and regulations on waste, considering more the global aspects of management and specific flows.

Over the years, so there was a strengthening of prevention and reduction of environmental impacts caused by the production and management of waste, Directive 75/442/EEC was being revoked for recovery of the waste in order to preserve natural resources.

In 1991, the Directive 75/442/EEC was change by two others Directive. At first, by Directive 91/156/EEC of the Council, 18 March, and at second by Directive 91/692/CEE of the Council, 23 December.

Directive 91/439/EEC had as a major goal changes to a high level of environmental protection, improve common terminology and definition of waste and redefine concepts. This directive was intended to end with differences in legislation between member states. It was decided that each member state should draw up waste management plans.

Considering the waste cycle (from production to disposal) and companies carrying out activities related to waste (collection, transportation or brokering) , the Directive sets it the withdrawal or recovery of waste by companies are required authorizations and supervision thereof , except for some stores that treat or recover waste , provided they comply with the requirements of environmental protection and are properly recorded .

Therefore, it was define that the disposal was made of self-sufficiently with the use of clean technologies and recyclable products, for measures to limit the production of

waste, taking into account market opportunities. It has chosen to invest in recycling and reuse of waste materials and the adoption of specific rules.

Directive 91/692/EEC has a sectoral basis and aims to streamline and improve the provisions relating to the transmission of information and publishing reports. This information and publications are related to European directives in the field of environmental protection.

It was considered appropriate to its revoked by Directive 2006/12/EC of the European Parliament and of the Council, April 5th, to limit the production of waste and the best way to organize your treatment and disposal.

The directive was again repealed by Directive 2008/98/EC of the European Parliament and of the Council, 19 November, to clarify and control the entire lifecycle of waste, from production to disposal, with emphasis on recovery and recycling; define waste, recovery and disposal, and strengthen measures to prevent waste. The current Waste Framework Directive (WFD) in force.

2.1.2 Legal framework in Italy

The first document about waste disposal was Leggi 20 marzo 1941, n. 366. In this law the topics addressed are collection, transportation and disposal of municipal solid waste.

However, the most important was the law "DPR 915", 5 September, 1982. This law was published to enforce Directive 75/442/EEC, about toxic and hazardous waste, and 76/403/EEC, concerning municipal waste.

DPR 915/82 lays down the general principles: the classification of waste; government's responsibility; general criteria pertaining to waste disposal, general criteria pertaining to questions of taxation, finance and sanctions; and dictates the responsibility of provinces and boroughs.

In 1984, the law was supplemented with regulations with reference to operating techniques were issued, in particular, classification of special waste as either municipal, toxic or hazardous. The waste was classified with respect to a list of toxic substances and the original production cycles (Carra and Cossu, 1990).

"Allow co-disposal in sanitary landfill MSW with other types of waste except special similar MSW (packing materials, wood shavings and material cutting); vegetable waste; sewage treatment which is stabilized as long as the content of metals and other toxic elements is not such as to require their classification as toxic and hazardous waste" (Carra and Cossu, 1990).

2.1.3 Legal framework in Portugal

The Portuguese Government made the first Decree-Law concerning waste management in 1927 (Decree-Law n.º 13166, 18 February). In this document, the municipal councils had the responsibility of refuse collection.

In general, the waste was only collected from the larger urban centres, and deposited in open uncontrolled landfill because the municipalities did not have any technical and financial conditions and the central government had no control over the matter.

In 1985, it published the first Waste Framework Law in Portugal, after approval of Decree-Law n. 488/85 of 25 November. This Decree-Law had action line in waste management based on the collection, storage, transport and disposal or utilization of waste. Were also defined the powers and responsibilities in the field of waste clearly, at central level, but also at local level.

According to the European Directives, his statements were being implemented. The Decree-Law 239/1997 came down the regulations is subject to waste management, including collection, transportation, storage, treatment, recovery and disposal, so as not to constitute a hazard or cause injury to human health or environment. In this law the term residue was defined as "any substance or object which the holder discards or intends or is required to discard" (Decree-Law 239/1997). Decree-Law 239/1997 was

determined to prepare five waste management plans: a nationwide, the National Waste Management Plan (NWMP) and four sectoral levels, the Strategic Management Plan of Hospital Waste (SMPHW), the Strategic Management Plan of Industrial Waste (SMPIW), Strategic Plan Management of Agricultural Waste (SPMAW) and Strategic Plan Management of Municipal Solid Waste (SPMMSW).

Several factors led to the replacement of the latter scheme 1997 for a new legal framework for waste management and implementing Directive 2006/12/EC. Decree-Law 178/2006 was approved. The repeal of Directive 2006/12/EC by Directive 2008/98/EC, the Decree-Law of 2006 was amended and the new Decree-Law 73/2011 was approved. Currently, it is the legal regime in force for waste management.

Waste management led to the passing of laws which permit the deposition of waste in landfills. Legislative Decree 152/2002, 23 May, was intended as a regular " installation, operation, closure and post-closure maintenance of landfills for waste, in order to prevent or reduce as far as possible negative effects on the environment or the local scale, in particular the pollution of surface water, groundwater, soil and the atmosphere, either on a global scale, in particular the greenhouse effect, as well as any risks to human health" (Decree 152/2002).

The Decree-Law 152/2002, 23 May, was amended by Decree-Law 183/2009, 10 August, which were defined " rules concerning the application of the legal regime now approved landfills already licensed or license as well as those relating to the duty to register and information on permits issued," but also updated " rules infraction under the provisions of the framework law on environmental offenses".

2.2 Uncontrolled landfill

Dump is a designation for a congeries of waste deposited indescribably and without control in a given location. In general, the waste is placed in unobtrusive locations, situated in mounted clearings or along the lines of natural drainage, and away from areas normally used by the populations (Levy and Cabeças, 2006).

Uncontrolled landfills are identical to dumps. They have sometimes a sealing layer of clay and are covered after closure.

However, have drainage system and treatment of leachates and burning biogas (Levy and Cabeças, 2006).

For a better understanding for the reader, it will be considered throughout this thesis the term "uncontrolled landfill" whether to “dumps” or to “uncontrolled landfill”, because neither have drainage system and treatment of leachates nor burning biogas.

The uncontrolled landfills do not have any operational control, causing negative environmental and social impacts.

Usually, uncontrolled landfills have the congeries of waste in auto-combustion resulting in the emission of noxious fumes and unpleasant odors (Levy and Cabeças, 2006).

It is common to do uncontrolled discharge and disorderly manner of waste and occurrences of harmful gases and leachate (Levy and Cabeças, 2006).

For suppress all negative impacts caused by uncontrolled landfills, it is necessary to develop a rehabilitation action and initiate foreclosure proceedings.

For star a rehabilitation action is an exhaustive survey of the characteristics of the zone, doing a preliminary analysis. For a complete closure of uncontrolled landfill, have to be done studies and observations to better planning and implementation of works. After all those procedure, the rehabilitation starts (Levy and Cabeças, 2006).

Preliminary analysis allows making better and more balanced choices. To this end, the following steps are performed:

1. Definition of the area limits to intervene;
2. Determination of the mass dimension of waste to confine, to model and to compact;
3. Topographic survey of the uncontrolled landfill area and a range of 25 meters wide surrounding;
4. Study of the morphology of the land underlying the fitting of the waste;
5. Observation of decomposition’ state of different waste disposal areas;

6. Analysis of waste mass situation (self-combustion zones and demarcation of them);
7. Uncontrolled landfills framework (surrounding vegetation, water lines affected or at risk, geology, hydrology, and resources; rainfall; life of the waste, etc.);
8. Planning and implementation of a plan of geological, geotechnical and environmental exploration (conducting surveys).

Following a thorough study of the uncontrolled landfill is the planning and deployment of actions to take. The project to closing the uncontrolled landfill should have control measures of pollution, such as:

1. Determining the points of onset and occur of leachate;
2. Determining the driving route and store leachate;
3. Location in the groundwater level;
4. Definition of geological and geotechnical characteristics;
5. Degree of combustion of the waste;
6. Volume setting of land covering;
7. Definition of volumetric modelling to print the waste;
8. Technical specifications (sealing and access);
9. Project funding, drainage and treatment system of leachate;
10. Project of drainage system and burning biogas;
11. Technical specifications for end cover closure and environmental protection.

The rehabilitation actions are divided in six phases (Levy and Cabeças, 2006).

The first action is cleaning, disinfecting and sealing the uncontrolled landfill. Before the cover, the area surrounding the uncontrolled landfill should be clean and compress to lead to decline population of animal harmful. To ward off the birds, networks or wire strands are placed; for rats, rodenticides are applied in three phases (preparation, placement of bait and maintenance by subculture campaigns). The gasket prevents animal harmful and unauthorized people from entering the area rehabilitated (Levy and Cabeças, 2006).

The second part of action is construction and rehabilitation of the access and modelling land. The new sections will allow access to the holes and sections of monitoring or

leachate to the feedback system. Pedestrian sections will facilitate the development of monitoring tasks. The modelling land allows the reduction of the volume of waste mass (containment and compaction), levelling the top of the slope and allowing placement of the cover material (Levy and Cabeças, 2006).

The third phase is to perform jobs that relate to the leachate and biogas. Initially, the drain is made of water and leaching restraint system with pre-treatment or final treatment. The leachate cannot be diverted to the water lines because of its high load. The leaching water can be diverted to a treatment plant wastewater with the ability to receive leachate or in-situ treatment plant (Levy and Cabeças, 2006).

The main factors to be taken into account for the planning and construction of the biogas extraction system are:

1. Compaction and settlement of uncontrolled landfill;
2. High groundwater level;
3. Condensation;
4. Gas quality.

The estimated production of biogas will be important for the measures to be taken. This production varies with the degree of decomposition and volume of waste deposited (Levy and Cabeças, 2006).

The fourth and fifth phases are final cover of uncontrolled landfill and rainwater drainage. The final cover is important for the reducing the volume of leachate and stabilization of biodegradation processes. Waterproofing layers are interleaved between layers of earth (clay, sandy material, gravel, sand) and geomembranes and geocomposite. The rainwater drainage allows rainwater to seep through drainage layer, reducing the pressures on the waterproofing system. The water is drained to a shackle concrete half-cane (Levy and Cabeças, 2006).

The last phase is the vegetal cover. The cover is part of the landscaping plan intervention, seeking to smoothly cover the uncontrolled landfill with the surrounding envelope. In the future the space can be leveraged for building sports infrastructure and recreational facilities (Levy and Cabeças, 2006).

After the closure of uncontrolled landfills must be adequate monitoring systems leachate, groundwater and biogas. The monitoring is possible by:

- Introduction of piezometers;
- Control of production and composition of leachate (sampling for analysis of pH, BOD, COD and conductivity);
- Control of settlements by leveling through superficial marks;
- Monitoring the biogas released by measuring the quantity and content of methane and carbon.

The recovery of a uncontrolled landfill always depends on each and has to take into account the specific conditions of the geographical region in which it operates (Levy and Cabeças, 2006).

2.3 Landfill

2.3.1 Definition

According Directive 1999/31/CE, 26 April, as define as "a waste disposal site for the deposit of the waste onto or into land (i.e. underground), including:

- Internal waste disposal sites (i.e. landfill where a producer of waste is carrying out its own waste disposal at the place of production), and
- A permanent site (i.e. more than one year) which is used for temporary storage of waste,

But excluding:

- Facilities where waste is unloaded in order to permit its preparation for further transport for recovery, treatment or disposal elsewhere, and
- Storage of waste prior to recovery or treatment for a period less than three years as a general rule, or
- Storage of waste prior to disposal for a period less than one year".

The landfill is a solution for waste disposal that cannot be seen simply, and can even be mistaken for a dump (Tchobanogluos *et al.*, 1993; Levy and Cabeças, 2006).

A landfill is facility of elimination used for the residual solid waste disposal in the surface (above or below) soils of the earth (Tchobanogluos *et al.*, 1993; Levy and Cabeças, 2006). It is an engineered facility for the disposal of waste designed and operated to minimized public health and environmental impacts (Tchobanogluos *et al.*, 1993).

They are environmental structures that require the involvement of a wide range of staff from different specialties during site selection.

The sanitary landfill, after balance, evaluation and approval, allows the development of construction of sanitary infrastructure in appropriate technical and environmental safety (Tchobanogluos *et al.*, 1993; Levy and Cabeças, 2006).

The weight rests on several factors which affect the calculating dimensions of landfill, ensuring technical, structural, environmental, economic, functional, health and social balance (Tchobanogluos *et al.*, 1993; Levy and Cabeças, 2006).

Also the phases of design, construction, operation and monitoring require the involvement of a wide range of staff from different specialties (Tchobanogluos *et al.*, 1993; Levy and Cabeças, 2006).

Even with the minimization in waste disposal at the final destination, the landfill will always be a solution, either at the end of the line as necessary of other waste treatment processes add either as a single treatment solution.

It is possible to position the landfill in the management of an integrated waste stream, either as a method of "treatment" of "disposal", "final destination" or "confinement".

Then, are presented the definitions of "treatment" and "disposal".

Treatment – "the manual, mechanical, physical, chemical or biological process of changing the characteristics of waste in order to reduce its volume or hazardous nature as well as to facilitate their transport, recovery or disposal after the sampling operations" (DL 183/2009).

"Disposal" – "operation aimed at giving an appropriate waste final destination pursuant to the legislation in force" (DL 178/2006).

These conditions are met by the landfill, since the treatment process ensures the degradation of the waste by internal physical and chemical reactions. Waste degradation by natural biological allows the definitive incorporation of mass compacted and stabilized in the printed spatial modelling to waste ground which serves as its foundation, until the mineralization level of the material biodegrades in place and stabilization confinement, and being solution of final destination. It is a framework adjusted to landscape integration of the landfill and safe use of this site after your closure.

2.3.2 Landfill age

It is possible to evaluate the age of a landfill in view of BOD/COD ratio, pH and the electrical conductivity.

According Tchobanogluos *et al*., *(*1993), checking the BOD/COD ratio of the leachate is possible the state of maturation of a landfill. The initial ratios will be range of 0,5 or greater. When the organic matter in leachate is readily biodegradable, the ratio in the range are 0,4 to 0,6. In a mature landfill (greater than ten years), the BOD/COD ratio is often the range 0,05 to 0,2.

Christensen *et al*. (2001), Öman *et al*. (2008), Yusof *et al*. (2009), Regardío *et al*. (2012) claim that in methanogenic phase the pH values increases and the BOD/COD ratio lowered a lot.

2.3.2.1 pH

As long the landfill age, the parameters suffer several changes (Qasin and Chiang, 1994). Values of the parameters concentration depend of the phase landfill. In initial anaerobic phase the leachate of the uncontrolled landfill shown low pH values (Qasin and Chiang, 1994; Bozkurt *et al*., 1999; Bozkurt *et al*., 2000). During the anaerobic phase and at end, pH increase beginning the humic phase with high pH, values between 8 and 9 (Bozkurt *et al*., 1999). Landfills in advanced level of maturity, pH values were higher, thus it is possible to say that the pH increase with the landfill age and the older

landfills tend to have leachates with higher pH (Qasin and Chiang, 1994; Regardío *et al.*, 2012).

The easily degradable organic compounds (volatile fatty acids and some heavy metals) present high concentrations in acid phase. Some secondary minerals are reactive, amorphous and metastable phases, and are sensitive to pH changes (Flyhammar *et al.*, 1999). According Yusof *et al*. (2009), the low pH at aerobic phase leads to increase the metal solubilisation due to the production of acid. This situation happens mainly in young and active controlled landfills.

According Bozhurt *et al*. (1999 and 2000) and Christensen *et al*. (2001), the variation of pH in the landfill phases are among 4,5-9; however, Qasin and Chiang (1994) establish the maximum value in 7. The illustrates Figure 2-1 the pH changes as well as changes in redox potential and gas composition during different phases in a landfill.

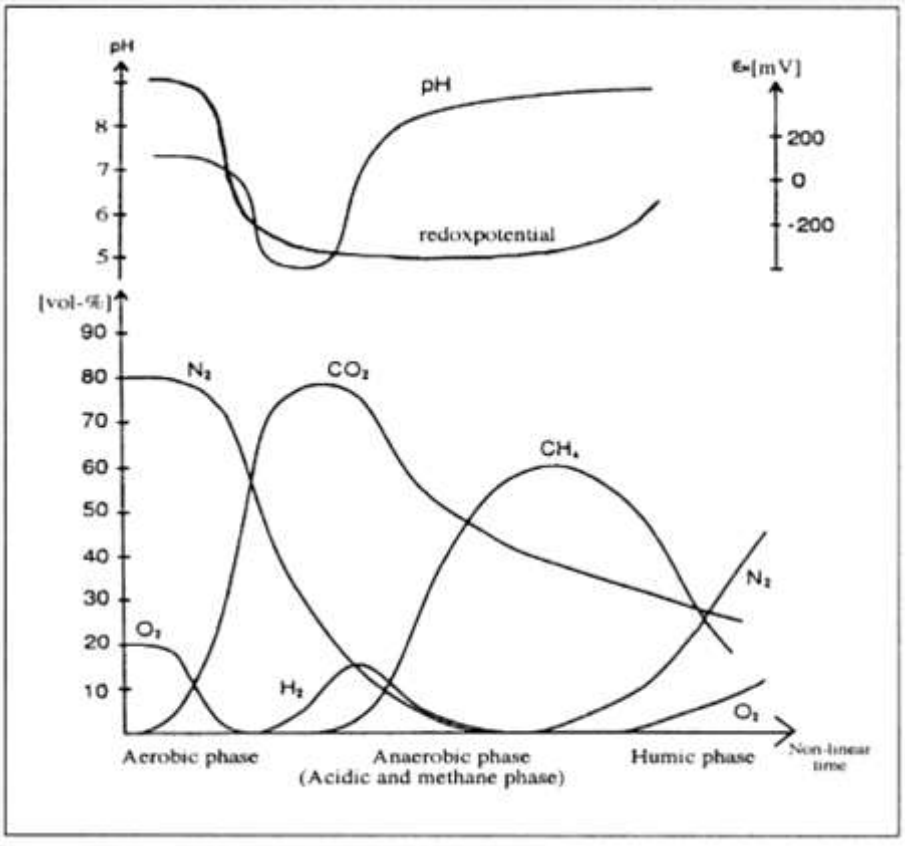


Figure 2-1 - Schematic illustration of the redox potential, pH (in pore waters) and gas composition during different phases in a landfill (Bozhurt *et al*., 1999; Bozhurt *et al*., 2000).

2.3.2.2 Electrical conductivity

Laner *et al*. (2011) evaluated the future emission in a MSW landfill in Austria (Breitenau), a controlled landfill with leachate extraction. In this case of study had verify that exist a linear correlation between electric conductivity and the leachate generation rate owing to a dilution processes due to the preferential flow within the landfilled waste (Fellner *et al*., 2009 and Laner *et al*., 2011). It is possible to say the leachate generation rate decreases as the electrical conductivity increases (Figure 2-2) (Fellner *et al*., 2009; Laner *et al*., 2011).

It was possible to establish this relationship because have been used 88 measurement points over 22 years (1988 to 2010) about leachate composition. To establish the correlation between the leachate discharge rate and electrical conductivity has been used to calculate the daily averages of different leachate parameters (e.g. Cl, COD, N-NH_4) (Laner *et al*., 2011). The logarithmic correlation was establish with collected monitoring data after the conductivity meters was installed at the ends of each of the three leachate collection pipes (Laner *et al*., 2011).

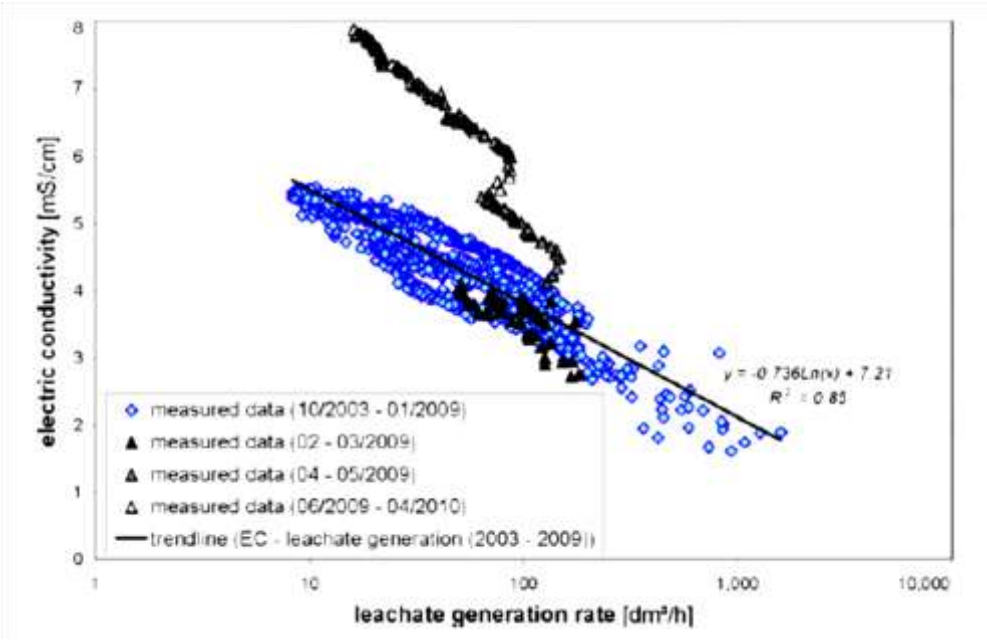


Figure 2-2 - Correlation between electric conductivity and the leachate generation rate (Laner *et al.*, 2011)

2.4 Leachate

2.4.1 Characterization

The mains problems caused by the waste disposal are precisely the formation of leachate waters, which drags down decomposition products and chemically active substances that can reach a watercourse or groundwater. The leachate cause serious pollution problems soil, water, and absence of a drainage system and collection of leachate waters (Martinho *et al.*, 2008).

The leachate can be defined as water based solution of compounds from the waste. It is a pollutant that percolated the waste material and was subject to physical, chemical and microbial processes (Qasin and Chiang, 1994; Christensen *et al.*, 2001; Øygard *et al.*, 2004).

It is possible to say the landfill's contaminants take the form of leachate after the water percolation (Bilgili *et al.*, 2008; Regadío *et al.*, 2012).

In general, the leachate has organic and inorganic compounds that may be dissolved or suspended and biodegradable and non-biodegradable in high concentrations (Christensen *et al*., 2001; Bilgili *et al*., 2008). The released of various contaminants from landfill migrate any pose a severe threat to surface and groundwater (Lu *et al*., 1985; Qasin and Chiang, 1994).

The waste disposal area must be considered in design and location of its potential pollution (Lu *et al*., 1985). This potential depends of various factors, divide in four characteristic groups, potential dangerous: dissolved organic matter (COD and TOC), inorganic macrocompounds (NH_4^+), heavy metals (Cd, Cr, Cu, Pb, Ni, Zn and Fe) and xenobiotic organic compounds (Christensen *et al*., 2001; Bilgili *et al*., 2007; Yusof *et al*., 2009; Regadío *et al*., 2012).

The variation of concentration of these compounds in the leachate depends of other factors as waste type (composition based on economic status of the country), quality of waste, climate, organic matter, landfill hydrogeological structure and operational conditions (Christensen *et al*., 2001; Bilgili *et al*., 2008; Regadío *et al*., 2012). On the other hand, the leachate has greater chemical composition variation depends of the age of the landfill's waste (Christensen *et al*., 2001; Bilgili *et al*., 2008; Regadío *et al*., 2012), physical waste characteristics, rate of water application and landfill depth (Lu *et al*., 1985).

The leachate volume generation is affected by four factors: water availability, conditions of landfill surface, condition of the waste and underlying soil conditions (Lu *et al*., 1985).

The principal source of the leachate generation is precipitation (rainfall and snowfall), provided contribution by irrigation. It is the main used to represent the total quantity of rain water that reaches the ground surface in a certain period of time (Lu *et al*., 1985).

The leachate generation can be calculated by a water balance which account for the volume of water entering and leaving the system in a period of time. The quantity of leached generated (L) can be calculated expeditiously by the equation 2.1. (Lu *et al*., 1985; Qasin and Chiang, 1994; IRAR, 2008).

$$L = P + U - ET + R_{ON} - R_{OFF} \quad [2.1]$$

L – Leachate generation

P – Input water from precipitation: in most cases, is the main source of leachate; There are four characteristics of rainfall that influence leachate generation (amount, intensity, frequency and duration);

U – Input water from underflow: Happens when the base of the landfill is located at a lower elevation of the water table of the surrounding terrain;

ET – Evapotranspiration: have physiological factors influence the characteristic of the vegetation, in addition to physical environmental factors;

R_{on} – Input water from surrounding surface runoff

R_{off} – Surface runoff

Different types of waste generate different types of leachate. MSW present higher concentrations of organic content, as TOC, COD, BOD (Christensen *et al.*, 2001). On the other hand, depending from author to author, the concentrations of the compounds in leachates were different despite the same type of the leachate. The MSW landfill can have the same constituents but not in the same percentage. Consequently, the values of the leachate generated were distinct country for country, region for region.

However, the production of leachate can be minimized preventing the time of water contact with the waste, using surface and subsurface drainage and a properly selected cover material (Lu *et al*, 1985). The concentration can have a variation of value between milligrams and micrograms (Moore and Ramamoorthy, 1984; Lu *et al.*, 1985; Christensen *et al.*, 2001, Öman *et al.*, 2008, Yusof *et al.*, 2009).

2.4.2 Leachate quality

The landfill leachate is considered by general public a source of pollution (Øygard *et al.*, 2004). It is possible to say leachate from landfill is an important source of ground

water pollution, doing the aquifer water lowers its quality (Lu *et al*, 1985; Qasin and Chiang, 1994).

In fact, it represents an impact for the water system either aquifers or surface water, because of the leachate percolated out of the landfill area (Øygard *et al.*, 2004; Thomsen *et al*., 2012). However, even with leachate treatment systems the compounds presented on the waste will be a concern (Yusof *et al.*, 2009).

In general, the concentration of the potential pollution compounds may be up a factor 1000-5000 times higher than groundwater concentrations (Christensen *et al.*, 2001).

The leachate quality is highly variable and depends of various factors that interacting with each other. The most important factors are type/characteristic and composition of solid waste, age of landfill, depth of solid waste, landfill design (e.g. size) and operation, rate of water application, the interaction of leachate with its environment, moisture content, degree of rainwater infiltration and temperature (Lu *et al*., 1985; Qasin and Chiang, 1994).

The composition of different landfills shows a large variation. Although, the most importants and significant factors which affect the composition of leachate are the age of the landfill and the degree of solid waste stabilization (Qasin and Chiang, 1994).

2.5 L/S ratio and mass-balance

To accelerate the metabolic processes of landfill (biochemical, chemical and physical) is necessary to increase the water flow in the system. It is possible to foresee of full-scale landfills data, relating the LSR results. Determining the amount of water (in liters) passing through a given waste mass (in kg dry matter of waste), commonly known as liquid to solid ratio (L/S ratio in l water/ kgDM). This L/S ratio is also used to determine the remaining pollution potential of MSW in landfills, as seen in Figure 2-3 (Fellner *et al.*, 2009). The evaluation of potential pollutant treating the values obtained

in a similar chart to that shown in Nevertheless, just around 40% pore water participates in advective solute transport in laboratory-scale simulation, whereas this is a fraction of the investigated full-scale landfill.

To estimate the possible pollution from the uncontrolled landfill is possible to make a mass-balance for heavy metals. The simulation is made to compare the content of metals in landfill leachate and estimation is made using average metal concentration in the leachate by the leachate volumes (Øygard *et al.*, 2004; Øygard *et al.*, 2005). The mass of leachate will be combining to a contaminant mass-balance, in other words, a chemical composition of landfill leachate (Thomsen *et al.*, 2012).

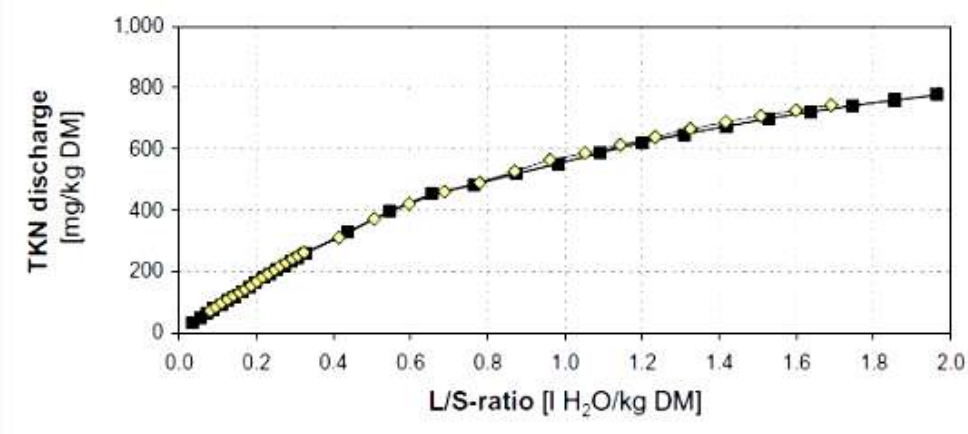


Figure 2-3 - Example of a graph to obtain after have the data (Fellner *et al.*, 2009)

2.6 Heavy metals

The heavy metals are, in general, an environmental problem for the water, surface and groundwater, in particular if they migrate in the leachate. It is a problem for the landfill operator if the leachate colleting is made prior to discharge (Bilgili *et al.*, 2007). Nevertheless, the heavy metals don't constitute a frequent water problem at landfill in part because usually the landfills have unassuming concentrations of these (Christensen *et al.*, 2001).

Cadmium in the environment has originated in industry, essentially from metallurgical and chemical industry, but also from mining. In its origin are also treatment facilities of hardware and electroplating. The carbon combustion, Zn, Cu and Fe metallurgy and agriculture are principals sources of cadmium (Moore and Ramamoorthy, 1984; Mendes and Oliveira, 2004). The stable state present in the natural environment is Cd^{2+} and it is commonly to found associated with zinc n the form of carbonates and sulphite ores (Moore and Ramamoorthy, 1984).

Cadmium is used in electroplating and used as pigments and to make batteries (Moore and Ramamoorthy, 1984).

The cadmium hydroxides and carbonates have a low solubility, being greatly reduced at pH values between 8 and 9. At pH 6 the ionic form is 96% of the total cadmium present in fresh water, as like chloride-complexes and sulphate-complexes. On the other hand, at pH 9 the ionic form represents only 47% and the complexes presents are mostly carbonates (Mendes and Oliveira, 2004).

No polluted water has a minimum content of cadmium below 1 µg/l in the most of the cases. Nevertheless, the concentration can reach 10 µg/l (Mendes and Oliveira, 2004).

Fresh water from human consumption may present high cadmium concentrations, due to contamination from the cover plumbing with this metal, welding made of silver and the use of galvanized steel tubing (Mendes and Oliveira, 2004).

Chromium is used in industry to make special steel. It is also used in treatment of surfaces in the manufacture of alloys, glass industry, textile industry, ceramics, glass, photography, wood preservation and leather tanning. Chromium is widely used as colorant. The effluent from this industry is quite contaminated (Mendes and Oliveira, 2004).

The most common forms in the environment are Cd^{3+} and Cd^{6+}. The sources of dust pollution are natural geological origin due to erosion of rocks rich in chromium. The chromium compounds are very unstable (Mendes and Oliveira, 2004).

In United States of America, the concentration of chromium is on average 14 µg/l. The waters are treated chromium concentration in the order of 5µg/l or lower. At pH 6 and at inorganic form, the free ionic form doesn´t exist. Its solubility is reduced and when the pH is lowered to its shape is cationic (Mendes and Oliveira, 2004).

Copper is a heavy metal present in environment in free form but also in sulphides, chlorides and carbonates batteries. The most common state is Cu^{2+}. It has a "wide variation in properties such as spectral, magnetic, complexing capacity and oxidation state" (Moore and Ramamoorthy, 1984). The metallic copper is very used for making alloys, the most of times brass and bronze (Mendes and Oliveira, 2004). The cooper is utilized in agriculture in the form of copper salts comprising insecticides, herbicides and algaecide. It is used in the same industry that chromium is used, particularly in the textile industry, photographic and ceramics (Mendes and Oliveira, 2004).

Copper may be identified in mammals (mammalian serum) as a blue protein – ceruloplasmin (Moore and Ramamoorthy, 1984).

According, community standards (Directive 80/778/CEE), the outlet of a water treatment plant, the recommended maximum value is 0,1 mg/l. Fresh water from human consumption the value is fixed in 2 mg/l (Mendes and Oliveira, 2004).

Iron is heavy metals exist in environment in solid state (Mendes and Oliveira, 2004). It is present is soil and rocks, in the form insoluble sulphate (iron pyrite) but also in the form of ferrous carbonate (soluble form). The main ores are magtite, hematite, chalcopyrite, marcasite and siderite (Mendes and Oliveira, 2004).

The different forms of iron in water depend of pH levels and dissolved oxygen content. At pH values between 4.5 and 9, the iron is usually in the form of ferrous ion. The mainly forms in fresh water are Fe^{2+} and the Fe^{3+} is present in very low quantities. In general, the groundwater in reducing conditions, the concentration of ferrous iron may have high value, with the maximum value of 10 µg/l (Mendes and Oliveira, 2004).

The iron mobility is in function of its valence state and its potential redox (Mendes and Oliveira, 2004).

Nickel is a heavy metal which is 0,001-0,016 % of the earth's crust and basic features cadmium (Moore and Ramamoorthy, 1984; Mendes and Oliveira, 2004). It possesses good thermal and electrical conductivity and hardness. It is a borderline element among hard and acid in chemistry interactions toward donor atoms as an acid acceptor (Moore and Ramamoorthy, 1984).

The major miners are hydrated silicates of magnesium and nickel. Nickel is used in industry as metal cover and as alloy and surface cover. It is used in glass and ceramics industry. Nickel has physical properties such corrosion resistance, durability over a wide range of temperatures and high strength (Moore and Ramamoorthy, 1984).

In fresh water, the most common form is the free ionic form (98%) at a pH value of 6, namely sulphate complexes. However, at pH 9, the free ionic form reduced until 9%, dominated the carbonate complexes (Mendes and Oliveira, 2004).

Lead is a heavy metal with amphoteric characteristics and has four stable isotopes (Mendes and Oliveira, 2004). It is classified as an intermediate acceptor among hard and soft acids in its interaction with ligands (Moore and Ramamoorthy, 1984).

Lead is used since three millennium b.C. and it has several uses including use in pavement, in jewellery, wine acidification with lead salts. The use of lead salts in feeding an exaggerated form led to many problems of chronic intoxication of humans (Mendes and Oliveira, 2004). Nowadays, iron is mainly used in metal products, storage batteries, pigments and chemistry (Moore and Ramamoorthy, 1984).

The mobility of lead is lower in oxidant conditions and even lower in reducing conditions. This low mobility is enhanced due to its great reactivity with organic matter, preventing their migration to groundwater when in soil (Mendes and Oliveira, 2004).

For pH with value 6, in freshwater, lead is in free ionic form (86%). pH 7, free ionic form represents only 9% of lead, the remainder are sulfate-organic complexes. The pH of 9 this amount is less than 1%, the remainder are carbonated complexes and complexes hydroxylated (Mendes and Oliveira, 2004).

The domestic and industrial effluents go to the hydrosphere about 15 $x10^9$ g/year. In the other hand, natural leaching is about 110 $x10^9$ g/year (Mendes and Oliveira, 2004).

Zinc is a heavy metal that is quite common in nature present in solid form (Mendes and Oliveira, 2004). Its normal occurrence is in localized deposits and has ease of extraction from ores (Moore and Ramamoorthy, 1984). Such as lead, zinc is an intermediate acceptor between hard and soft acids in its interaction with ligands (Moore and Ramamoorthy, 1984).

The principal ore of zinc (zinc sulphate) occurs along with lead deposits and it is used by industry due its chemical and metallurgical properties. It is mostly used in galvanizing iron and steel products. Nowadays, zinc is used in construction, automobile and building industries (Moore and Ramamoorthy, 1984).

At pH 7, free ionic form represents 95% of zinc (organic and inorganic), the remainder are complexes of ion SO_4^{2-} or is linked to free radicals. At pH 9, free ionic form represents only 6% of zinc (Mendes and Oliveira, 2004).

2.6.1 Mobilization of heavy metals

Authors as Bilgili *et al*. (2007) reported large variation in heavy metals concentrations from different landfill and in most of times low concentrations. The concentrations are low in the leachate as well because of four control processes in landfill leachate plumes as such sorption, precipitation, complexation and oxidation-reduction reactions (Christensen *et al.*, 2001; Bilgili *et al.*, 2007). The processes involved in the heavy metals attenuation in leachate plumes are at Table 2-1. The results were obtained after rigorous separations perform of two samples of leachate-polluted groundwater from Vejen Landfill (Denmark) plume. The speciation calculation perform was made on the truly dissolve fraction because, on the other hand, "purpose of identifying in detail the various metal species in leachate plumes is not possible, because in some investigations small colloids have been included in the dissolved fraction" (Christensen *et al.*, 2001).

The variation of the concentration depends primarily on of the waste composition, the landfill technology and variation of the seasons (summer and winter).

Table 2-1 - Summary of processes involved in attenuation of heavy metals in leachate plumes adapted from Christensen *et al.* (2001)

Process	Cd	Cr	Cu	Pb	Ni	Zn
Dilution	+	+	+	+	+	+
Complexation	+	+	++	++	+	+
Redox processes	-	-	-	-	-	-
Sorption	+	+	+	+	+	+
Precipitation						
Sulfhides	+	-	+	+	+	+
Carbonates	+	-	-	+	-	+
Other	+	++	+	+	-	-

The authors Bozkurt *et al*. (2000) and Bilgili *et al*. (2007) concluded the concentration of heavy metals in the leachate decrease with the age of landfill. In conclusion, pH has great influence in the solubility of the metals (Bozkurt *et al*., 2000).

In the works of Christensen *et al*. (2001), Bilgili *et al*. (2007) and Öman *et al*. (2008) the values founded and with which they worked are in levels of μg/l. The rates are Cd 0-24 μg/l, Cr 0-188 μg/l, Cu 5,8-240 μg/l , Fe 160-170 400 μg/l, Ni 9,8-91 μg/l, Pb 0-100 μg/l and Zn 13-28 800 μg/l.

According Bilgili *et al*. (2007), studying the mobilization of heavy metals in partly stabilized landfill during the oxidation with air, allows found pH buffer capacity of partly degraded MSW was high enough to maintain alkaline leachates during the experiments. There the possibility for unexpected high concentrations and mobilization rates of heavy metals during the oxidation of the most reactive phases of sulfides; the organic matter is low, as well. With environmental changes from anaerobic to an

aerobic, the speciation of the heavy metals may change. However, the aqueous concentrations in leachate are not anticipated to increase significantly. In the low pH conditions of a landfill, heavy metals (cadmium, copper, iron, manganese and lead) can dissolve and migrate with the leachate. Though other chemical reactions can change the state of heavy metals as well, allowing them to attack to other particles and travel with leachate. In experiments can be use an experimental columns in the different conditions, anaerobic and aerobic.

For Christensen *et al*. (2001), part of the metal species is the colloidal metals and organic and inorganic complexes. The colloids present in the leachate in terms of organic and inorganic particles in the size range of 0,001 μm. The heavy metals content of leachate samples was too low for determining colloidal species. The author concluded that it is complicated to discuss the attenuation mechanisms in aquifers with the presence of the metal species in leachate. This happens because the metal species may have different behaviour and redistribute can be different as well. On the other hand, the attenuation mechanisms that only concern free divalent metal ions are the most of the information known. It is proven the attenuation of heavy metals will have the influence of significant heavy metals in plumes by increasing metals solubility and mobility.

2.6.2 Sorption, complexation and precipitation

When it comes to sorption, it is possible to relate reaction such as adsorption, adsorption, surface complexation, surface precipitation and ion exchange (Lu *et al*., 1985; Moore and Ramamoorthy, 1984; Christensen *et al*., 2001; Bozkurt *et al*., 1999; Bozkurt *et al*., 2000). The processes involved in landfill are represented in the Figure 2-4. Compounds such as organic matter, especially humic materials, and oxides of Fe, Mn and Al, negatively charged are sorption for divalent metal cations due to its high affinity (Baird, 1995; Christensen *et al*., 2001). In many studies only a few sorption of heavy metals onto aquifer materials in the presence of a leachate matrix and measured

a linear sorption isotherms for Cd, Ni and Zn in presence of water samples collected at 7 m downgradient from a landfill in Denmark (Vejen Landfill) (Christensen *et al.*, 2001).

According Christensen *et al*. (2001), the distribution coefficient, K_d, the equilibrium between the sorbed metal and the metal in solution, increase significantly with pH. The author suggests that complexation increase metal mobility mainly at high pH-values and the major sequences of the complexation are found at low pH-values. In this case, the velocity of metals migration could be 5% to 20% faster than the groundwater flow velocity. The compounds with minor migration velocity, with increasing pH values, are Cd, Ni and Zn. Although, the Cu complexation increases with the pH, being the migration velocity major.

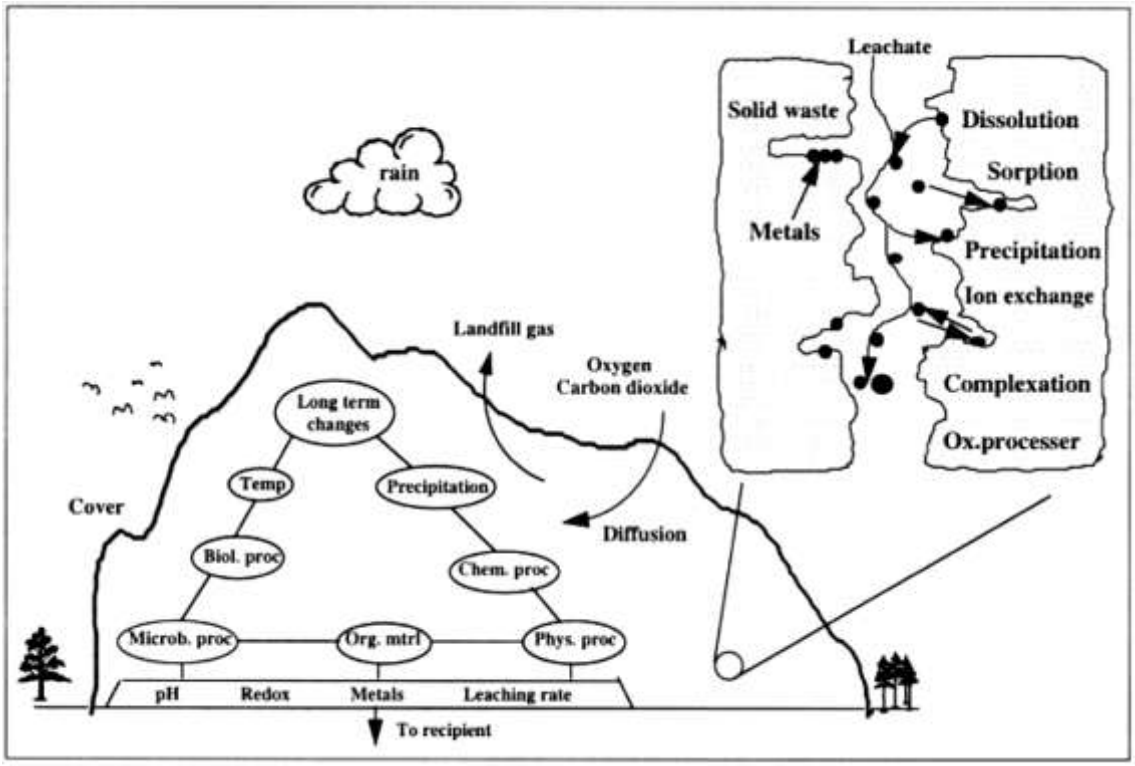


Figure 2-4 - Schematic illustration of processes in a landfill (Bozkurt *et al*., 2000)

The solubility of the heavy metals, such as Cd, Ni, Zn, Cu and Pb, in the leachate plumes may be governed by carbonates or sulphites. The precipitates governing the solubility of heavy metals are very difficult to assess in relative in very complex solutions included the landfill leachate.

However, carbonates and sulphites are presumably the most important precipitates. The precipitation of metals may have to address in general terms because the precipitation reactions may be relatively slow, take months to establish equilibrium.

Precognition of solute equilibrium concentration in terms of free metals ions is very uncertain. This due to of possible supersaturated and uncertainty about the composition of the controlling precipitate and solubility of products of precipitation.

2.7 Organic matter

Organic matter is a matter composed of carbon (45-55%), oxygen (35-45%), hydrogen (3-5%) and nitrogen (1-4%) compounds that have come from the remains of once-living organisms (such as plants or animals) and their waste products in the environment.

Organic matter is present throughout the ecosystem. Organic matter forms molecules that contain nutrients as it passes through soil and water; after degrading and reacting, it can then move into soil and mainstream water. Organic matter acts as a buffer, when in aqueous solution, to maintain a less acidic pH in the environment.

MSW also have constituted organic matter which represent 50-60% of total of waste. When water percolated the waste, the organic matter is entrained in the water, which can be detected in the resulting leachate. Depending on the maturation state of the landfill, that is, the degree of decomposition of the waste contained in it, the leachate has different values for compounds of carbon and nitrogen. This variation depends on the amount of organic matter, aerating conditions, but especially the pH. During the

acid phase, the leachate samples present a low pH and the concentration of TOC and heavy metals are high (Tchobanoglous and Kreith, 2002). On the other hand, during the methane phase, the pH range from 6,5 to 7,5 and TOC and heavy metals are lower (Tchobanoglous and Kreith, 2002).

Over the degradation processes, the remaining substrate becomes more resistant to degradation, low biological activity and humic phase moves toward its conclusion. The organic matter is transformed into more stable compounds than the parent compounds (Bozkurt *et al*., 2000). The organic matter when decomposed or decomposing has constituted essentially of carbon compounds. After the humic phase, the organic matter was degraded throughout and is very stable (Bozkurt *et al*., 1999). Gradually, their redox potential decreases due to aerobic and anaerobic degradation (Bozkurt *et al*., 1999).

To evaluate the organic matter in the leachate samples, analyses are performed, for example, TOC, TKN and NO_3.

The organic matter in the water body can be quantified by determining chemical or biochemical consumption of oxygen or the oxidability. It is possible to determine the organic load present by measuring the Total Organic Carbon (TOC) (Mendes and Oliveira, 2004).

The TOC present in particulate form or in solution is organic and volatile or non-volatile, natural and synthetic compounds. TOC is a good evaluation methods of organic substances because it determines the carbon content present in the leachate, whether resulting from anthropogenic activity, whether of humic substances (that form in soils) whose concentration varies with the season and volume of water percolated or infiltrated into the ground (Mendes and Oliveira, 2004).

Nitrogen is present in four compartments of the planet: the earth's crust, terrestrial ecosystems, aquatic ecosystems and the atmosphere. Most of the nitrogen is not included in the Earth's crust is present in the air (99,96%). On the other hand, the

nitrogen in the aquatic ecosystem is diverse and 95,2% is presented in soluble form (47,9% of nitrogen is organic) (Mendes and Oliveira, 2004).

Nitrogenous substances present in water bodies are from the biodegradation of organic waste and excretions (animal and human), and municipal waste and industrial effluents, agricultural waste and leachate, landfill leachate, adjuvants some detergents and substances by rainwater (Mendes and Oliveira, 2004).

The assembly of nitrogen compounds in the water can be determined Total Kjeldahl Nitrogen (TKN) based on the oxidation in acidic medium and distillation of ammonia (Mendes and Oliveira, 2004).

Nitrogenous organic compounds can be assessed by determining the concentration of NO3 (reduced species). Nitrates are highly soluble and are present in leachate.

3 Cases of study

3.1 Simulated aerobic and anaerobic pilot scale landfill reactor

Predict emissions from a landfill can be simulation based on laboratory experiments. It is possible to compare by field investigation. The experiment can have analysis of waste composition and the operation can perform with landfill simulation bioreactors. According Fellner *et al*. (2009) landfill simulation bioreactors were applied to evaluate and optimize stabilization methods for a landfill as "flushing bioreactor" or in-situ aeration. The landfill simulation bioreactors were constructed using column with 40 cm diameter and 80 cm height (Fellner *et al*., 2009).

In experimental work of Bilgili *et al*. (2007), landfill bioreactors were constructed from columns of polypropylene made with 50 cm diameter and 200 cm height. Bilgili (2007 and 2008) used a second layer around the bioreactor, with 60 cm diameter, and the blank between these two layers was filled with heat isolation material to prevent temperature redistribution between the bioreactors and the surrounding environment. The bioreactors were filled with 15 cm of gravel drainage, 170 cm of solid waste and more gravel drainage. The gravel was with perforated pipe to collected leachate samples between one or two weeks intervals. The leachate samples were collected when discharging leachate from the landfill bioreactors and stored between 4°C (Bilgili *et al*., 2007) and 5°C (Östman *et al*., 2006) in plastic bottles. The quantity of discharged leachate for each bioreactor was measured and then stored in a refrigerator to use for recirculation. Leachate was recirculated using a peristaltic pump located at the top of the recirculated bioreactors. Each column was used to simulate a different landfill concept. The aeration was performed by a compressor. That was connected to the aeration pipes at the bottom of bioreactor (aerobic ones). According Bilgili *et al*. (2007 and 2008), air was introduced at the bottom of the waste and passed through the waste in an upward direction. This procedure helped the perforated pipe introduced in each aerobic bioreactor, with 60 cm diameter and 120 cm length. Thus, the aeration performance was increased.

The experimental landfill bioreactors can have others dimensions, as 40 cm diameter and 70 cm length. The aeration can be continuous with an "air flow of 3 l air/h, with (1 l/kgDM d)" (Hrad *et al.*, 2013).

According Hrad *et al*. (2013), the aeration in situ of landfill has been recognized for its potential to convert conventional anaerobic landfill into biological stabilised state, accelerating organic matter degradation under aerobic conditions. In this case both current and potential emissions of the landfill waste are mitigated, in long term. It is possible to shorten the time and the effort necessary for post-closure management. Exist two ways to aerate: high pressure or low pressure. The high pressure is generally used to minimise explosion danger and odour annoyance during landfill excavation. It is used to landfill mining projects, as well. The low pressure is frequently used and recognised for its potential towards landfill remediation aimed at accelerated biological waste stabilisation.

An aerobic bioreactor concept is normally implemented to increase the operating lifetime of landfill. The recovering capacity is more quickly and leachate treatment costs are reduced (Hrad *et al.*, 2013). The last effect of waste stabilisation, after the aeration completed, as the aerobic degradation potential of previously and anaerobic operated waste material was assessed in laboratory experiments at same period. The landfill simulation bioreactors were dividing in two different condition; ones were operated in anaerobic conditions at all experiment and the others into an anaerobic phases (1/10 of the total time) at first and after in an aerobic conditions.

3.2 Study with different waste streams - MSW, industrial waste, slag and ash, RCD – in an uncontrolled landfills

In an uncontrolled landfill, a risk of contamination from leachate is predictable, unless exist a clay layer on the landfill bottom with more than 45% sheet silicates of illite-smectite type (Regadío *et al.*, 2012). Uncontrolled landfills are without appropriate

bottom liners and without leachate collection systems (Yusof *et al.*, 2009). This is a critical problem for soil and groundwater protection and both can become contaminated (Yusof *et al.*, 2009; Regadío *et al.*, 2012). It is impossible to know what all the pollutants are in an uncontrolled landfill. Amongst leachate pollutants, the main substances of concern are organic substances, ammonia nitrogen and heavy metals (Yusof *et al.*, 2009).

The uncontrolled MSW landfills study by Yusof *et al*. (2009) in Malaysia has the classification level 1 – controlled tipping. Yusof *et al* (2009) shows that the uncontrolled landfills had a lower concentration of COD than the active controlled landfills with a difference of 10 times upper. The BOD/COD ratio was low as same as on the closed controlled landfill. The lower value of the BOD/COD ratio is typical in old landfill on the methanogenic phase. The heavy metals values had concentration between the values of the active controlled and closed controlled landfills. The metals values observe at uncontrolled landfill were fairly low; it is possible due to the metals' adsorption onto the clay or humic substances produced from the degradation of waste. The highest concentrations were Fe, Mn and Al, as like in active controlled landfill. The results of Yusof *et al*. (2009) study were in agreement with other studies done in Indonesia (Leuwigadja, Bandung) and Thailand (San Sai, Chian Mai) by Robison (2007) and Taiwan by Fan *et al.* (2006). The results were from leachate samples taken from the methanogenic phases. Yusof *et al*. (2009) verifies that uncontrolled landfill had the slightly higher organic contents than the landfills. Nevertheless, the other parameters like the ammonia-nitrate were similar compared with Thailand and Indonesia, but higher than those Taiwan. Yusof *et al*. (2009) concludes that the impact of the leachate from the uncontrolled landfill was the worst. However, the negative impact on the freshwater systems was also observed on the other landfills, due to landfill surface runoff or to improper treatment being practiced (Yusof *et al.*, 2009).

Regardío *et al*. (2012) made a study examining old uncontrolled landfills in Spain, one in northeast (L1) and two in centre of Spain (L2 and L3), which received mixed municipal solid and industrial wastes. The three landfills were mature (had more than ten years). The results of the leachate samples analyses shown low concentration of

dissolved oxygen, which indicates the landfills were in anaerobic conditions and the redox potential reduced. The concentrations of the heavy metals were low with value below 1 mg/l. The values can be seen at Table 3-1.

Table 3-1 - pH and heavy metals values adapted from Regadío *et al*. (2012)

Parameters*	**L1**	**L2**	**L3**
pH	7,2	7,9	6,7
Cr	0,04	0,83	0,03
Pb	0,43	< 0,10	< 0,10
Zn	0,32	< 0,02	0,10
Cd	< 0,02	< 0,02	< 0,02

* the parameters were measured in mg/l, except pH.

As like others studies as Christensen *et al*. (2001) and Öman and Junestedt (2008), Regadío *et al*. (2012) concluded that had a relationship between the pH and the age of the waste; pH increases with over the years of the landfill. On the other hand, the chemical oxygen demand and the biological oxygen demand suffer a decrement. The ratio of the BOD/COD suggests that the landfills were in the final anaerobic-methanogenic stage but the values are low. Regadío *et al*. (2012) also confirmed that the electrical conductivity and the dissolved solids decrease with the landfill age, although these reductions happens, as a result of the fluctuation between the wet and dry seasons, over the time BOD and COD have variation values. The landfill corresponding to a higher mixed industrial and municipal solid waste had the higher concentration of sodium and chloride than the other landfills, due to less organic charge of the industrial waste than the municipal waste. The landfills with more urban waste, receiving less industrial waste, had higher concentrations of organic matter and lower concentration of heavy metals (Regardío *et al*., 2012).

In general, a MSW landfills have an enormous emission potential. However, this potential has to be evaluated to make a better leachate management. In case of a MSW landfill the parameters most analysed are pH value, electrical conductivity, COD, BOD, TOC, AOX, BTEX, N-NH_4, TKN, N-NO_2, N-NO_3, SO_4, P, Cl, Na, Ca, Mg, K, Fe, Cd, Ni, Pb, Zn, and some other heavy metals. The compound with higher concentration in the leachate was the nitrogen-ammonia. The first solid waste analyses show a high total pollution potential. Nevertheless, only an insignificant part (7%) of the total potential nitrogen-ammonia load has been released till the last sampling in 2011. The fraction of released nitrogen reaches a value between 10% and 30%; so it is possible to say "that the majority of the pollution potential remains inside the landfill, indicating the long-term significance of this substance pool" (Laner *et al.*, 2011). At the same time, the increase of the nitrogen-ammonia can be justified the installation of a new cover.

On the other hand, the change in the water flow paths, leads to a continuous decrease in the leachate generation rate and accordingly an increased of the compounds concentration of the leachate due of the water that bypassed in zone of solution and degradation processes and of the increased availability of mobilizable substances. In conclusion, a high concentration of the compound must be expected in the leachate for long time periods because the final cover installation hampers a fast decrease of the leachable substance potential taking part in the water flow regime (Laner *et al.*, 2011).

In the study of an uncontrolled MSW landfill in Malaysia, Yusof *et al*. (2009) corroborate that the active controlled landfill had higher organic contents than the closed controlled landfill. Consequently, the BOD/COD ratio in the active controlled landfill is higher as well, reflects it being of the acetogenic or aerobic phase (Lee *et al.*, 2010). But for the closed controlled landfill, the BOD/COD ratio is lower and represents a typical feature of the methanogenic phase of an old landfill (Levy and Cabeças, 2006; Yusof *et al.*, 2009).

The both controlled landfills had a high concentration of ammonia nitrogen. The active controlled landfill had this concentration due to the hydrolysis and fermentation of organic nitrogen. With these processes of solubilisation continue and the soluble

nitrogen increase but the inorganic nitrogen contents had a low concentration, corresponding to the anaerobic phase of waste decomposition (Yusof *et al.*, 2009).

The active controlled landfill had a high heavy metals concentration (Yusof *et al.*, 2009; Laner *et al.*, 2011), in particular Fe, Mn and Al (Yusof *et al.*, 2009).

In comparison with the results of the study in Spanish landfills that received industrial and municipal solid waste (Regardío *et al.*, 2012) it is possible to verify, in general, that the value were lower than the other studies, especially relating to pH, inorganic macrocomponents and heavy metals (Christensen *et al.*, 2001, Öman and Junestedt, 2008, Regadío *et al.*, 2012).

Øygard *et al.* (2005) concluded that the MSWI bottom ash lead to higher rate of heavy metals than MSW landfills (except for Fe and Zn). The Table 3-2 illustrated the variation of compounds concentration in the MSW and MSWI bottom ash landfills.

Table 3-2- Concentration of the leachate's parameters adapted from Oygard *et al.* (2005)

Parameters*	**MSWI bottom ash landfill (maximums values)**	**MSW in the same area (maximums values)**
Fe	1,4	150
Cd	2,8	0,31
Pd	31	6,3
Hg	0,26	0,02
Cr	500	56
Cu	290	26
Ni	64	25
Zn	58	410

* the parameters were measured in µg/l, except Fe that was measured in mg/l.

According Wang *et al.* (2012), the study of the potential for leachate from construction and demolition waste in column experiments shown that quality characteristics of the leachate collected fell within the typical range of construction and demolition waste comparing with others field measurements and laboratorial experiments.

The comparisons of different studies for leachates of C&D of measured parameters are described at Table 3-3.

Table 3-3 - Comparison of measured C&D leachate parameters adapted from Wang *et al.* (2012)

Parameters	**Melendez (1996)**	**Weber (2002)**	**Jang (2003)**	**Jambeck (2004)**	**Dubey (2005)**	**Wang (2012)**
pH	6,95	6,90	7,00	7,00	7,00	6,40
Fe (mg/l)	36	1,65	-	-	-	<0,01
Ar (µg/l)	12,3	41,1	380	38,1	300	<4,0

The increase of alkalinity along the experiment indicates a shift in the construction and demolition debris layer from oxidizing to reducing conditions (Wang *et al.*, 2012).

4 Methodology

4.1 Waste Samples

Both landfills are site in the North-East of Italy, in a village near Verona.

The "Noè-Tebaldi" landfill is the oldest one; it is an uncontrolled landfill, and with no detailed information concerning its characteristics. The site was a gravel quarry, with a superficial extension of about 12.000 m^2. When excavation ended, they filled the site with waste. Waste disposal started in the '70s and it ended at the half of the '80s. Approximately, they disposed 100.000 m^3 of different type of waste (MSW, foundry sands, demolition waste, etc.).

The "Servizi Costieri" landfill operated in the period 1988-1993. Differently from the previous one, it is a (slightly) controlled landfill: there's a bottom liner (1 m of clay), a top cover (0,2-1 m of clay), but no leaching colleting system. The site has a superficial extension of about 13.000 m^2 and they disposed 90.000 m^3 of foundry sands.

The characterization carried out for these two sites consisted in 10 drillings (5 drillings for each site), located as described in the attached file. All the drillings were performed until reached the natural soil underlying waste.

Five samples were extracted from each landfill. The samples were called V1, V2, V3, V4, V5 for the “Noè-Tebaldi” landfill, and SC1, SC2, SC3, SC4, SC5 for the “Servizi Costieri” landfill. The position of the sampling has been decided in order to obtain the maximum variability of the waste contained in each landfill. Each sample was taken with a probing from the ground level up to the depth of 10-15 meters. In a later phase, the samples were been completely mixed up and sieved (20 mm) in order to collect a sample for soil analysis. Every sample contained only the 2-3 % of inerts residues that were discharged to obtain a more representative sample.

A schematic representation of sampling until the process construction of the bioreactor can be seen in Figure 4-1.

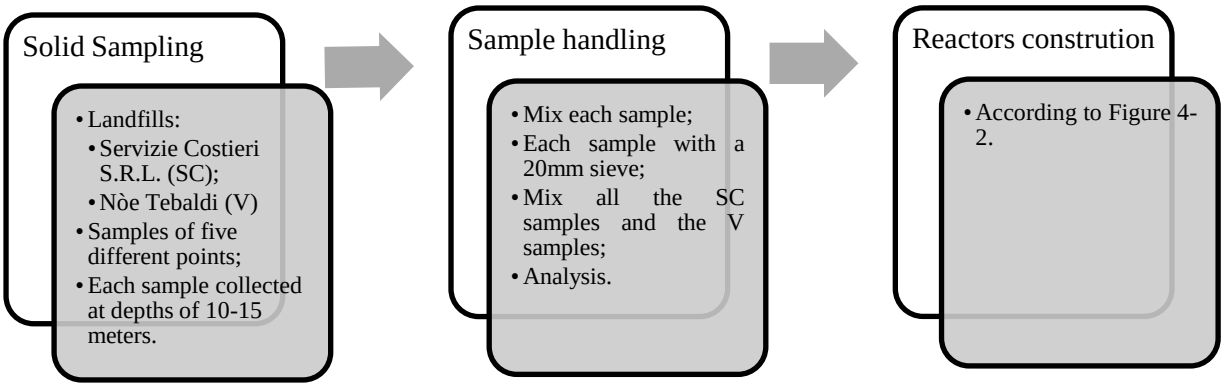


Figure 4-1- Scheme of the solid samples collection

It was observed in situ that the V2 sample was reached the groundwater level. On the other hand, the SC5 samples showed the presence of unidentified material aggregate in yellow little blocks.

4.2 Reactor preparation and other equipments

For the experiment were used columns made out of plexiglass. The bioreactors were sealed on the top and on the bottom.

The upper end has two valves (with certification of operation), one of them permits the extraction of air and the other allows the introduction of water and leachate (if necessary). To improve a better distribution of the liquids (fresh water or leachate), a perforated tubular ring was put at the top of the column. The lower end is equipped with tap allow leachate extraction and the introduction of air into the bioreactor.

The columns with the samples VmixA and VmixB have an internal diameter of 250 mm and a height of 1000 mm. The columns V2, SC5, SCmix have an internal diameter of

100 mm and an effective height of 800 mm. In all columns, a 100 mm thick gravel layer (gravel particle size 10-15 mm) was placed at the bottom of each bioreactor for leachate drainage and at the top to better distribute the liquids. A sketch of the bioreactors is represented in Figure 4-2.

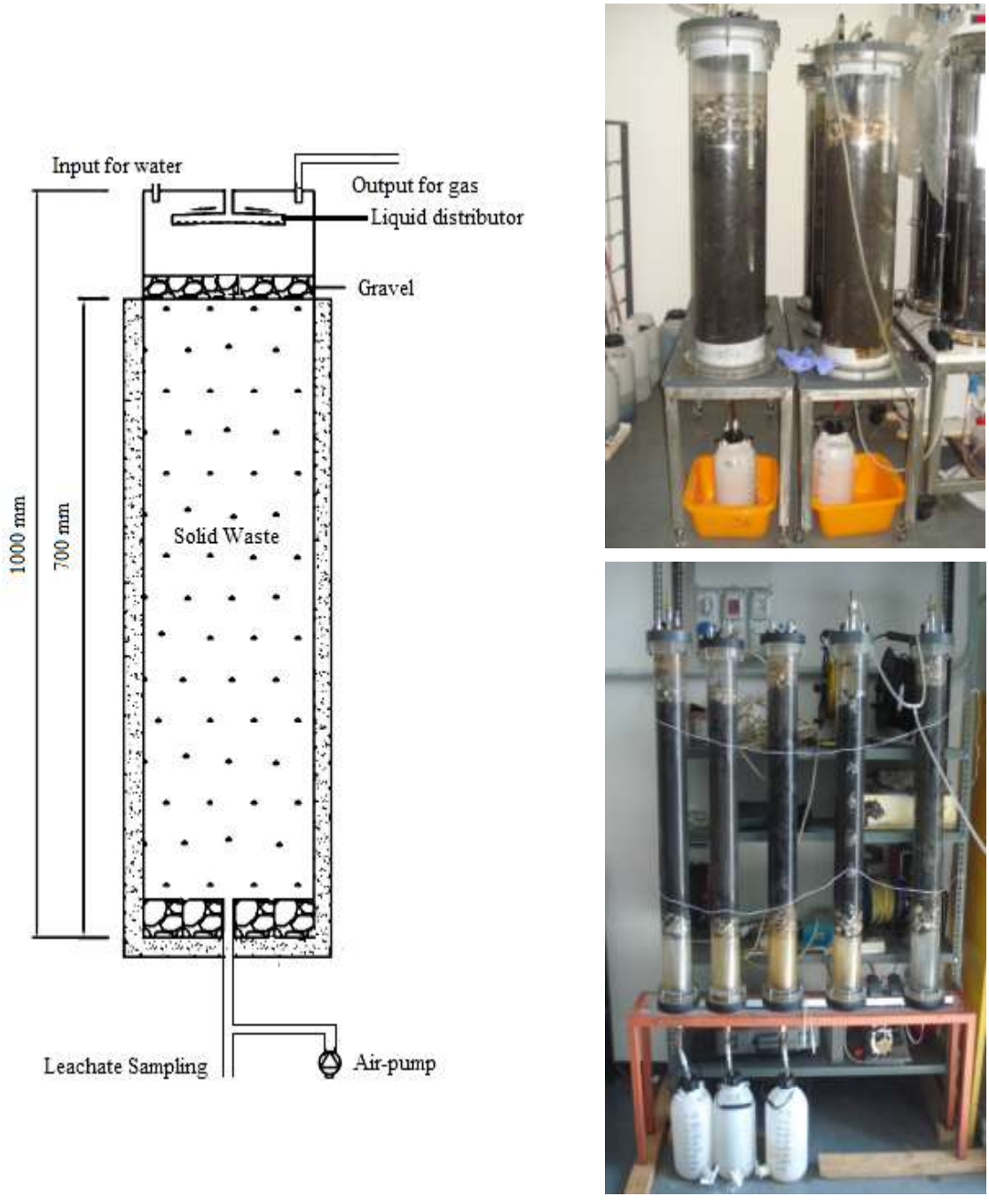


Figure 4-2- Scheme of a landfill simulation bioreactor and all the bioreactors with leachate collecting system

The bioreactors were operated under anaerobic and/or aerobic conditions. When they were operated under aerobic conditions, air was introduced into the system by RESON® Air-pump AC-9601 (VmixB) and BOYU® S-9901 (SCmixB and V2B) (Figure 4-3). The emissions from columns under aerobic conditions were sent out of the operating room through a PVC pipe. This pipe was connected to the air outlet valve installed on the top of the column (Figure 4-4).

Figure 4-3 - Inlet air of the aerated system

Figure 4-4 - Overview of air outlet pipes

4.3 Selection of parameters for analysed

The first solid samples were sent to the external laboratory EETI. This preliminary analysis, along with analyzes made in the laboratory LISA was possible to verify which components to take into account for the analysis of potential pollutants at the level of the leachate. See Table 4-1.

The first collection of leachate was also analyzed by both laboratories. The analysis were done to choose the parameters able to evaluate, parameters that reported values above the voltage limit of the measuring instrument. The choose for analysis heavy metals to evaluated were Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn, As, Hg and organic fraction to evaluate were TOC, TKN and NO_3, since they are the most common being analyzed in cases of identical study.

The parameter chosen to support this study was pH, because it is influenced by the age of the landfill, and has influence on the mobilization of metals and organic matter.

Table 4-1 - Analyses of the solids samples after handling and mixing the original sample

Parameters	V2		Vmix		SC5		Scmix	
	Lisalab	EETI	Lisalab	EETI	Lisalab	EETI	Lisalab	EETI
TS (%)	82	82,8	86	84,3	88	87,3	90	90,3
TOC (%Css)	1,82	-	1,73	-	1,75	-	1,11	-
TKN (mgN/kgDM)	1469	-	2095	-	664	-	921	-
N-NH4 (mgN/kgDM)	530	-	313	-	664	-	921	-
IR4 (mgO2/gDM)	0,72	-	0,74	-	-	-	-	-
Cd (mgCd/kgDM)	1,67	-	2,02	-	0,54	-	1,39	-
Cr (mgCr/kgDM)	131	-	284	-	145	-	38,7	-
Cu (mgCu/kgDM)	102	-	471	-	157	-	67,5	-
Fe (mgFe/kgDM)	40905	-	39405	-	91867	-	24167	-
Mn (mgMn/kgDM)	410	-	316	-	1308	-	558	-
Ni (mgNi/kgsDM)	64,4	-	48,3	-	64,2	-	25,2	-
Pb (mgPb/kgDM)	155	-	233	-	122	-	562	-
Zn (mgZn/kgDM)	467	-	350	-	126	-	450	-
As (mgAS/kgDM)	0,80	-	0,32	-	0,36	-	0,63	-
Hg (mgHg/kgDM)	0,62	-	7,31	-	35,20	-	0,26	-
Formaldehyde (mgHCHO/kg ui)	-	17,6	-	8,8	-	11,9	-	8,1
Hydrocarbons C<12 (mg/kgDM)	-	60,73	-	7,9	-	20,73	-	18,18
Hydrocarbons C>12 (mg/kgDM)	-	576,79	-	121,17	-	< 5	-	17,6
Boro (mgB/kgDM)	-	7	-	3	-	4	-	3
2-chlorophenol (mg/l)	-	< 0,02	-	< 0,02	-	< 0,02	-	< 0,02

Table 4-2 - Analyses of the solids samples after handling and mixing the original sample (continuation)

Parameters	V2		Vmix		SC5		Scmix	
	Lisalab	EETI	Lisalab	EETI	Lisalab	EETI	Lisalab	EETI
2,4-dichlorophenol (mg/l)	-	< 0,01	-	< 0,01	-	< 0,01	-	< 0,01
2,4,6-trichlorophenol (mg/l)	-	< 0,001	-	< 0,001	-	< 0,001	-	< 0,001
Pentachlorophenol (mg/ l)	-	< 0,001	-	< 0,001	-	< 0,001	-	< 0,001
2-methylphenol (mg/l)	-	0,01	-	0,01	-	0,01	-	0,01
3-methylphenol (mg/l)								
4-methylphenol (mg/l)								
Phenol (mg/l)	-	< 0,01		< 0,01	-	< 0,01	-	< 0,01
Amines Total (mg/l)	-	0,028	-	0,028	-	0,028	-	0,028
IPA (mg/l)	-	72,7	-	47,9	-	10,5		5,65

4.4 Work planning – Experimental procedure

For the experiment was set up seven bioreactors: VmixA, VmixB, V2A, V2B, SC5, SCmixA and SCmixB. V2 and SC5 are filled with waste deriving from samples V2 and SC5, respectively. These two samples were chosen for the experimental work, since they have different characteristics from the others samples. Bioreactors called VmixA, and VmixB derive from the mixing of V1, V2, V3, V4 and V5, and SCmixA and SCmixB and SC1, SC2, SC3, SC4 and SC5. In each column the waste is composed both of under sieve and coarse material.

Each column was used to simulate a different landfill concept and the operational conditions used are given in Table 4-3. The conditions presented are intended to provide L/S ratio equivalent in all the bioreactors, as to ensure equivalent conditions as aerobic conditions in aerated bioreactors.

Table 4-3 - Operational conditions used in the bioreactors to simulate different landfill conditions

Bioreactors	**Operating condition**	**Refuse (kg)**	**Airflow (l/min.)**	**Water input (l/week)** (7 weeks)	**Initial L/S ratio** (l H2O/ kgDM)
VmixA	Anaerobic	52,5	-	4	0,14
VmixB	Aerobic	52,5	1,8	4	0,14
V2A	Anaerobic	7,5	-	1	0,34
V2B	Aerobic	7,5	2	1	0,34
SC5	Anaerobic	7,5	-	1	0,32
SCmixA	Anaerobic	7,5	-	1	0,31
SCmixB	Aerobic	7,5	2	1	0,31

The first waste characterization has been taken from the under sieve of each sample, their weight was two kilogram and was analyzed the following parameters: TS (%), TOC, TKN, N-NH3. The heavy metals were been analysed as well; the compounds were: Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn, As and Hg (Table 4-1).

Until the field capacity was reached, the bioreactors were filled with distilled water and its recirculation was made. In that phase, all the bioreactors were run under anaerobic conditions.

After the field capacity is reached, the columns were completely saturated, in order to simulate the worst case and to produce leachate (Qasin and Chiang, 1994). This happens when the groundwater levels grows up and saturate the waste in the landfill. The water was maintained in the bioreactor for two weeks. The controlled samples were collected of the bioreactors after these two weeks.

The bioreactors VmixA, V2A, SC5 and SCmixA were maintained in anaerobic conditions and used as controls, to compare the results with the bioreactors in aerobic conditions. In a second phase, the bioreactors VmixB, V2B and SCmixB stars to be in aerobic conditions. The experimental procedures are described at Figure 4-5.

The aeration of the bioreactor VmixB was made with a pump flow of 1,8 l/min about 8 hour per day (work days, in total of 10 days). Following the aeration of the VmixB bioreactor, was put at VmixA and VmixB 0,8 l of fresh water, in a total of 8 l for two weeks. The fresh water percolated the waste, washing it and accelerated the metabolic processes (Fellner et al, 2009). The samples are collected in sealed bottles. Collections of samples were made every day and the samples correspond at fresh water addicted the day before. The leachate samples of the day were transferred to the accumulated samples' bottle. The accumulated samples of one week were analysed, having two analyses per cycle of 15 day (10 days of sampling). Were realised three cycles, in a total of six weeks and six analysis. The experimental procedures of VmixA and VmixB are described at Table 4-4.

Before being saturated, the bioreactors V2B and SCmix B were aerated two week (ten days) 8 hours per days. The flow pump is about 2 l/min. After these two weeks of aeration, bioreactors were saturated as the others. The controlled samples were collected of the two bioreactors after two more weeks. Behind the samples collecting, started a new aeration cycle. Every week the bioreactors V2B and SCmix B were aerated about 8 hours per day. After five days, was added 1 l of fresh water on the bioreactors V2A, SC5, SCmixA, V2B and SCmix B. Were performed four cycles of one week. The experimental procedures of V2A, SC5, SCmixA, V2B and SCmixB are described at Table 4-5.

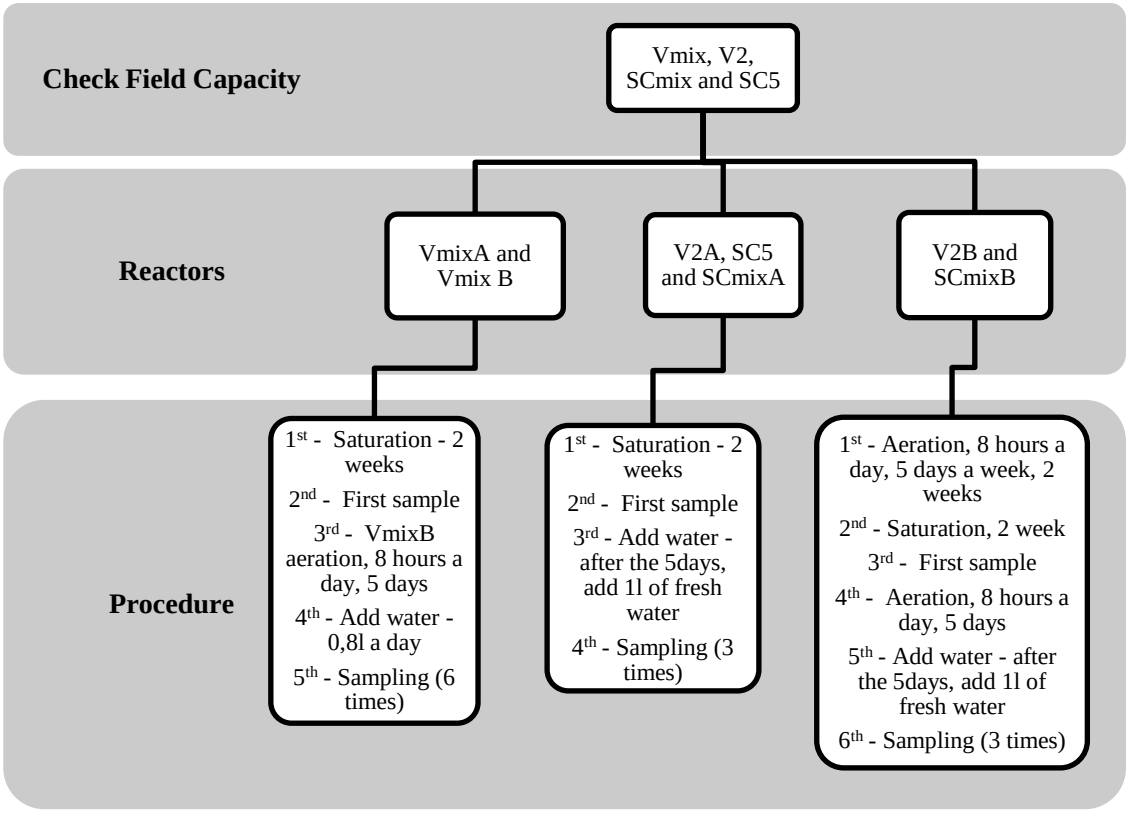


Figure 4-5 - Scheme of all the Experimental procedure

The bioreactors which are smaller than the VmixA and VmixB, was opted to add 1 litre of water per week, in contrast to 4 litres in bioreactors VmixA and VmixB, to maintain a similar proportion of fresh water to be added for dry matter all bioreactors. Thus the maximum water added was collected in the form of leachate, minimizing losses during

the sampling process, was chose to add water at the end of each week of aeration. On the other hand, the contact time may have been compromised.

The air pumps were installed on the bottom of the bioreactor, the same exit for the leachate sample. The pump and the bioreactor were connected with an aeration pipe.

Table 4-4 - Procedure for a week of bioreactors VmixA and VmixB

Actions in order	Sampling for analysis	Sampling	Aeration (VmixB)	Add water
1st Day	☑	-	8 hours	0,8 l
2nd Day	-	☑	8 hours	0,8 l
3rd Day	-	☑	8 hours	0,8 l
4th Day	-	☑	8 hours	0,8 l
5th Day	-	☑	8 hours	0,8 l

The samples of all bioreactors were collected and put at plastic bottles and lay in the fridge at a temperature between 4-5°C for further analysis. Each week is possible to determine an L/S ratio. It is possible to present the leachate concentration as a function of L/S ratio. This model allows estimating the evolution of leachate quality within the emission projections under different conditions (Laner *et al.*, 2011).

Along the experiment, the bioreactors had been working at room temperature.

The analyses were done for the following compounds: pH, TS, TOC, TKN, NO_3, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn, As and Hg.

Table 4-5 - Procedure for a week of bioreactors V2A, V2B, SC5, SCmixA and SCmixB.

Actions in order	Sampling for analysis	Aeration (SCmixB; V2B)	Add water
1st Day	☑	8 hours	-
2nd Day	-	8 hours	-
3rd Day	-	8 hours	-
4th Day	-	8 hours	-
5th Day	-	8 hours	1 l

4.5 Methods of analysis of the leachate

The efficiency of the experimentations was evaluated by measuring organic and inorganic parameters. The influent and effluent samples were performed following Italian analytic standards for water and wastewater samples (CNR-IRSA, 29/2003).

4.5.1 pH

The pH is measured with a pH meter, after a calibration with two buffers at pH 4 and pH 7 (IRSA-CNR 29/2003).

4.5.2 Total Solids

The total solids correspond to the solids that remain in a sample its evaporation in an

oven at 105°C for 12 hours. On the other hand the volatile solids correspond to the solids that remain in the dry sample after thermal treatment in a muffle at 550°C for 3 hours (IRSA-CNR 64/84).

4.5.3 TOC

The TOC is the result of the difference between the TC, total carbon, an the IC, inorganic carbon. Both these parameters are obtained oxidising the sample with air in a combustion tube in the presence of a catalyst: the carbon dioxide produced is quantified with an infrared detector. The difference in obtaining TC or IC is the working temperature (higher for TC) and the acid pre-treatment of the sample in the IC procedure, for transforming all the carbonate and bicarbonate in carbon dioxide (IRSA-CNR 29/2003).

The samples were analysed filtrated in case of presence of suspended solids.

4.5.4 TKN

With this analysis it is possible to measure the sum of the organic nitrogen and the ammonia present in a sample. Measuring separately the ammonia and subtracting the amount from the TKN value it is possible to obtain the organic nitrogen.

A sample is refluxed in strong sulphuric acid solution in the presence of a catalyst. At the end of the digestion all the nitrogen (organic and ammonia) is transformed in ammonium ion. All ammonium ions are then changed in ammonia, increasing the pH with sodium hydroxide, and it is distilled in steam current. The stripped ammonia is collected in a boric acid solution and titrated with a standard sulphuric acid solution (IRSA-CNR 29/2003).

4.5.5 Nitrates

The evaluation of nitrates is carried through colorimetric determination with sodium salicylate (IRSA-CNR 29/2003).

4.5.6 Heavy metals

The heavy metals are detected in an ICP-OES (spectrometry), after the digestion and filtration of the sample. The first operation carried out in a strong acid solution, allow the break of metal bonding with the organic matter; the second permit not to have particulate in the sample to be analyzed (IRSA-CNR 29/2003).

4.6 Processing data

To estimate future landfill emissions, different conditions in landfill must be considered. The effect of the different conditions on future landfill emissions is illustrated via different scenarios.

For calculated the total mass extracted of the contaminant was used the equation:

$$C * V \text{ ext., mg or } \mu g \qquad [4.1]$$

C – Concentration of the parameter

V – Volume of the extracted leachate

The mass of the contaminant inside the bioreactor (mass of the contaminant that is inside the column) was calculated by the equation:

$$C * (FWinput + WHC), \text{ mg or } \mu g \qquad [4.2]$$

C – Concentration of the parameter

FWinput – Fresh Water inputted

WHC – Water Hold Capacity of the moment

The mass balance of the contaminant is calculated in order to represent:

Mass/kg DM, mg/kg DM or µg/kg DM

M – Total mass of the parameter extracted and exist in the leachate

kg DM – kilogram of dry matter in the bioreactor

This L/S ratio was used to determine the remaining pollution potential of MSW in landfills:

TotalFW/kg DM

TotalFW – total of fresh water collected in the bioreactor

kg DM – kilogram of dry matter in the bioreactor

5 Results and discussion

5.1 Leachate pH

The leachate pH evolution from bioreactors in aerobic conditions may be seen at Table 5-1.

Table 5-1 - pH values from bioreactors in aerobic conditions

Samples (week)	VmixB	SCmixB	V2B
1st	7,2	7,5	7,4
2nd	7,5	8,2	7,7
3rd	7,0	8,2	8,2
4th	7,7	-	-
5th	8,2	-	-
6th	8,0	-	-
7th	8,2	-	-
8th	8,1	-	-

The leachate pH evolution of the bioreactors in anaerobic conditions may be seen at Table 5-2.

Table 5-2 - pH values from bioreactors in anaerobic conditions

Samples (week)	VmixA	SCmixA	V2A	SC5
1st	7,4	7,7	7,4	7,7
2nd	8,7	7,7	7,4	7,8
3rd	8,6	7,8	7,2	7,6
4th	7,8	-	-	-
5th	8,0	-	-	-
6th	7,7	-	-	-
7th	7,6	-	-	-
8th	7,5	-	-	-

In the bioreactors in aerobic conditions, VmixB, SCmixB and V2B, had pH values increase 7 to 8.

The VmixB start with pH value 7,2. Summarizing, increase at long of the time, except in one sample (the third one wherein the pH value was 7,0).

The bioreactors SCmixB and V2B start with pH values of 7,5 and 7,4, respectively. The last (third) sample present the same value for both bioreactors, 8,2.

The bioreactors in the anaerobic conditions present pH values 7,4 and 8,7. The VmixA start with a pH value of 7,4. The last sample has value 7,5. The SCmixA and SC5 first sample present pH value of 7,7. The V2B start with 7,4 pH value. The last sample present a decreasing in V2A and SC5, 7,2 and 7,6, respectively.

One of the most important parameter affecting the metal concentrations in the leachate landfill is pH (Bilgili *et al.*, 2007). Considering the diversity of the waste on the two landfills in the study, it is possible to say the waste contain in its composition soils (inorganic) and organic matter. On the other words, both landfills in study contain a

complex mixture of different compounds with variable chemical and physical properties (Bozhurt et al., 2000).

The increase of values in aerobic bioreactors indicates that the bioreactors are working in similar conditions as the reactors in the experiment of Bilgili *et al.* (2007), in other words, pH increased and reached to 8.

In the aerobic or acetogenic phase, the pH reaches approximately 7,5, a value that decrease till the beginning of anaerobic phase, reaching pH values between 4,5-5,5 (Bozhurt *et al.*, 1999; Bozhurt *et al.*, 2000). The anaerobic phase which divides in acid phase and methanogenic phase has varying pH values among 4,5-5,5 and 9, respectively (Christensen *et al.*, 2001; Bozhurt *et al.*, 1999; Bozhurt *et al.*, 2000).

For the bioreactors that not being aerated is possible to say, based on studies carried out by Christensen (2001) and Bilgili (2007 and 2008) the pH values describe the phase of anaerobic or the final of methanogenic phase. The pH values were 7 to 8.

The pH value of the leachate bioreactor in anaerobic conditions among 7,2 and 8,7, indicated the rapid degradation of solid wastes in aerobic conditions (Bilgili *et al.*, 2007).

According Christensen *et al.* (2001), for a leachate from a old uncontrolled landfill, the pH values in methanogenic phase were among 7,5 and 9, as the results obtain for the anaerobic bioreactors.

5.2 Heavy Metals and organic fraction in the leachate

Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn, As and Hg concentrations of leachate samples collected from bioreactors are given at Table 5-3, Table 5-4, Table 5-5, Table 5-6, Table 5-7, Table 5-8 and Table 5-9, and TOC, TKN and NO_3 concentrations of leachate samples collected from bioreactors VmixA and VmixB are given at Table 5-3 and Table 5-4.

The analyses of the heavy metals show low concentration in the order of μg/l and the organic fraction in order of mg/l.

Table 5-3 - Leachate values of VmixA

Samples (week)	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	As	Hg	TOC	TKN	NO_3
	μg/l										mg/l		
1st	< 10	25,6	71	4820	382	81,2	< 30	114	< 1	5,6	213	161	143
2nd	< 10	21	112	1046	304	105	< 30	264	< 1	0,46	124	143	131
3rd	< 10	< 20	624	886	310	210	< 30	3600	< 1	< 0,2	92,4	132	123
4th	< 10	28,8	64,6	1000	220	199	< 30	166	-	-	71,3	118	113
5th	< 10	26	49,2	632	139	262	< 30	189	-	-	60	113	109
6th	< 10	25,4	36,2	2120	175	354	< 30	322	-	-	51,9	118	112
7th	-	-	-	-	-	-	-	-	-	-	71	101	108
8th	-	-	-	-	-	-	-	-	-	-	46,9	115	111

Table 5-4 - Leachate values of VmixB

Samples (week)	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	As	Hg	TOC	TKN	NO_3
	μg/l										mg/l		
1st	< 10	< 20	24,2	1442	554	115	< 30	44	< 1	14,1	170	140	134
2nd	< 10	< 10	580	1996	918	204	< 30	1106	< 1	< 0,2	69,4	133	123
3rd	< 10	< 10	624	886	712	210	< 30	3600	< 1	< 0,2	44,3	89,6	86,8
4th	< 10	< 10	290	28,4	460	518	< 30	2200	-	-	36,1	11,2	7,56
5th	< 10	< 10	278	34,8	136	102	< 30	1586	-	-	34,8	2,8	1,12
6th	< 10	< 10	488	43,6	24,8	900	< 30	1424	-	-	33,6	5,32	0,84
7th	-	-	-	-	-	-	-	-	-	-	36,1	4,76	0,05
8th	-	-	-	-	-	-	-	-	-	-	27,4	0,5	-

Table 5-5 - Leachate values of SCmixA

Samples (week)	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	As	Hg
	μg/l									
1st	< 10	< 10	27,4	112	270	110	< 30	167	< 1	79
2nd	< 10	< 10	< 20	48,2	110	222	< 30	106	< 1	79
3rd	< 10	42,2	71,6	200	79,4	216	< 30	242	-	-

Table 5-6 - Leachate values of SCmixB

Samples (week)	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	As	Hg
	μg/l									
1st	< 10	< 10	< 10	41,2	144	29,2	< 30	60.4	-	-
2nd	< 10	< 10	< 20	121	55,2	38,6	< 30	21	-	-
3rd	< 10	49	< 20	510	24,4	< 20	< 30	< 50	-	-

Table 5-7 - Leachate values of V2A

Samples (week)	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	As	Hg
	μg/l									
1st	< 10	< 20	< 10	3120	492	804	< 30	54,6	1,2	21
2nd	< 10	< 10	< 10	1694	110	302	< 30	35,8	-	-
3rd	< 10	44,2	< 10	1630	113	185	< 30	46,8	-	-

Table 5-8 - Leachate values of V2B

Samples (week)	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	As	Hg
	μg/l									
1st	< 10	< 10	106	4640	1328	972	< 30	268	-	-
2nd	< 10	< 10	44	83	137	2020	< 30	196	-	-
3rd	< 10	46,8	103	92,6	95,4	882	< 30	185	-	-

Table 5-9 - Leachate values of SC5

Samples (week)	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	As	Hg
	μg/l									
1st	< 10	< 10	< 10	240	1068	129	< 30	94	< 1	3540
2nd	< 10	< 10	< 10	98,2	155	87,2	< 30	120	-	-
3rd	< 10	41,6	< 20	142	34,4	58	< 30	127	-	-

The concentration should decrease as long as the waste washes. All the data are given as L/S ratio (Table 5-10), indicating the amount of fresh water passing through the waste and in order to compare results of different bioreactor scales.

Cd, Cr, Pb, As and Hg concentration of leachate samples collected are not shown because the values obtained in the analyzes were below the voltage limit of the measuring instrument. Hence, it is not possible to obtain the exact concentration of the compound neither relate it to L/S ratio.

SCmixA, SCmixB, V2A, V2B and SC5 had low concentration values in the three samples taken.

Cd, Cr, Cu, Pb, As and Hg concentration of leachate samples collected in SCmixA, SCmixB, V2A, V2B and SC5 were below the strain limit of the measuring instrument. Hence, it is not possible to conclude the real emissions for the specific compounds.

Table 5-10 - L/S ratio values throughout the experimental work

Samples (week)	VmixA	VmixB	SCmixA	SCmixB	V2A	V2B	SC5
	l H_2O/kg DM						
1st	0,117	0,125	0,720	1,080	0,739	0,945	0,828
2nd	0,228	0,326	1,033	1,393	1,082	1,288	1,153
3rd	0,322	0,328	1,189	1,549	1,254	1,460	1,315
4th	0,415	0,421	-	-	-	-	-
5th	0,508	0,513	-	-	-	-	-
6th	0,601	0,606	-	-	-	-	-
7th	0,694	0,698	-	-	-	-	-
8th	0,788	0,791	-	-	-	-	-

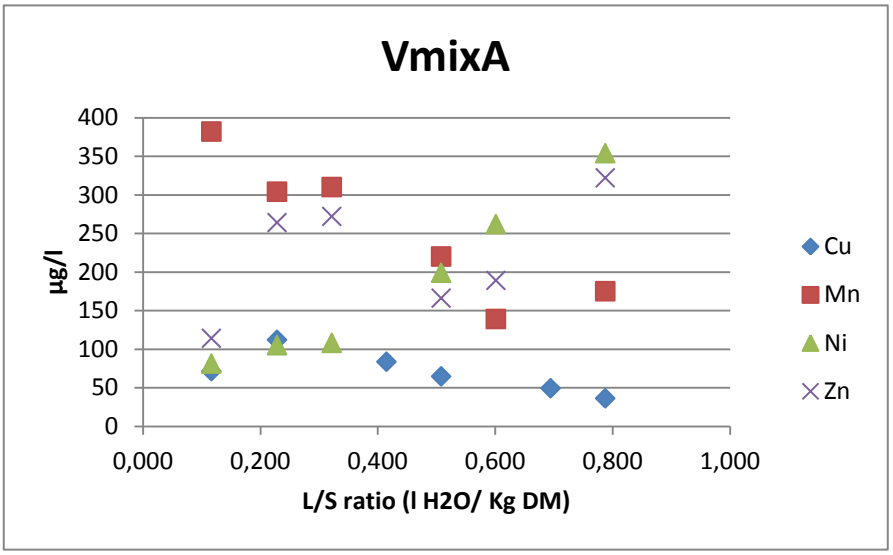


Figure 5-1 - Values of metals concentration from VmixA and VmixB

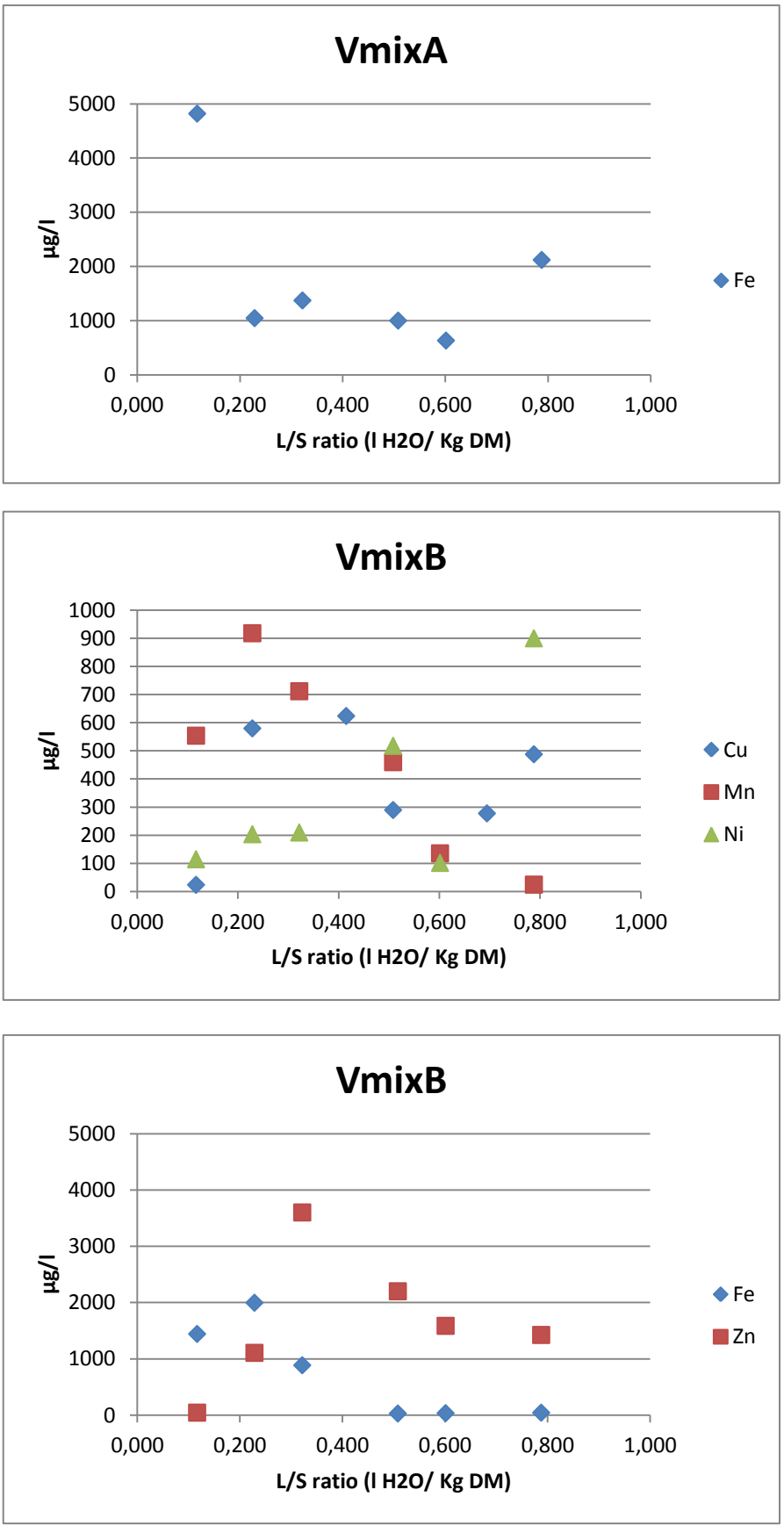


Figure 5-2 - Values of metals concentration from VmixA and VmixB (continuation)

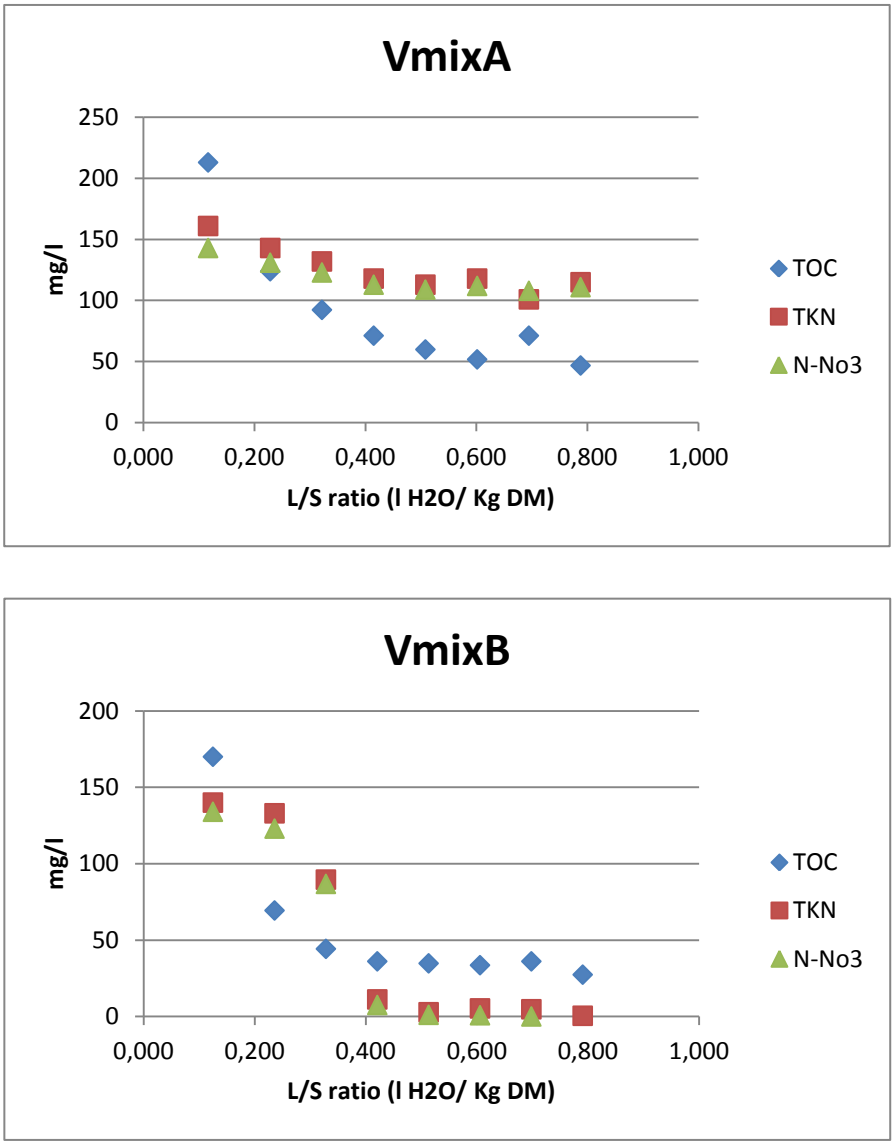


Figure 5-3 - Values of organic fraction concentration from VmixA and VmixB

The most significant values are from the VmixA and VmixB.

The heavy metal concentrations as a function of L/S ratio shows that as this ratio increases, not always the concentration decreases, possibly even increase (see Figure 5-1 and Figure 5-2). The organic fraction (TOC, TKN and NO_3) as a function of L/S ratio shows a decrease of concentration as long as the L/S ratio increase (see Figure 5-3).This fact may be due to variations in time of contact between waste and water added. It was expectable that the concentrations were decreased, which was observed for both the heavy metals either for the organic fraction. With model concentration

versus L/S ratio, it is possible to estimate the evolution of leachate quality in different types of waste in different bioreactor conditions (Laner *et al.*, 2011).

According Christensen *et al.* (2001), Bilgili *et al.* (2007) and Öman *et al.* (2008), metals concentration in the leachate, including heavy metals, can be low and may be associated with high values of pH, which enhance sorption and precipitation. Over the years, after closure of the landfill, the amounts of heavy metal concentrations ranging down to values close to micrograms per litre, and can reach the value zero after twenty years (Lu *et al.*, 1985).

Solid waste includes organic matter and soils have significant sorptive capacity especially at high pH values (Bozkurt *et al.*, 1999; Bozkurt *et al.*, 2000; Bilgili *et al.*, 2007).

According Bozhurt *et al.* (1999 and 2000), the organic compounds can be very strong sorbents for many of the leached metals and retard their escape from the landfill. According Baird *et al.* (1995), humic materials have a great affinity for heavy metals cations. The metal release that takes place during the methanogenic phase is probably to a large extent caused either by release of metals complexed to organic matter or by the release of solid particulate forms transported with the water from the deposit as small particles or colloids. Christensen *et al.* (2001) said in his study "the heavy metals was associated with colloid content of leachate".

The discharge limit to sewer systems imposed by Italian and Portuguese legislation is given in the Table 5-11.

All the compounds concentrations were below the discharge limit to sewer system, except one value of Fe equal to 4820 µg Fe/l, first samples of VmixA. Zn values in VmixB were above the Italian discharge limit; only the first sample was below of this limit.

Table 5-11 - Wastewater discharge limits to sewer systems

Parameter (mg/l)	Discharge limit	
	Italian D.Lgs 152/99	Portuguese DL236/98
Cu	≤ 0,4	1
Fe	≤ 0,4	2
Mn	≤ 0,4	2
Ni	≤ 0,4	2
Zn	≤ 0,1	-

5.3 Total emission – potential pollution

Emissions of bioreactors with two different types of waste from two landfills were estimated for Cu, Fe, Mn, Ni and Zn (see Figure 5-4 and Figure 5-5). Cd, Cr, Pb, As and Hg concentration values obtained in the analysis are below the strain limit of the measuring instrument. Other parameters were considered relevant were TOC, TKN and NO_3 (see Figure 5-6).

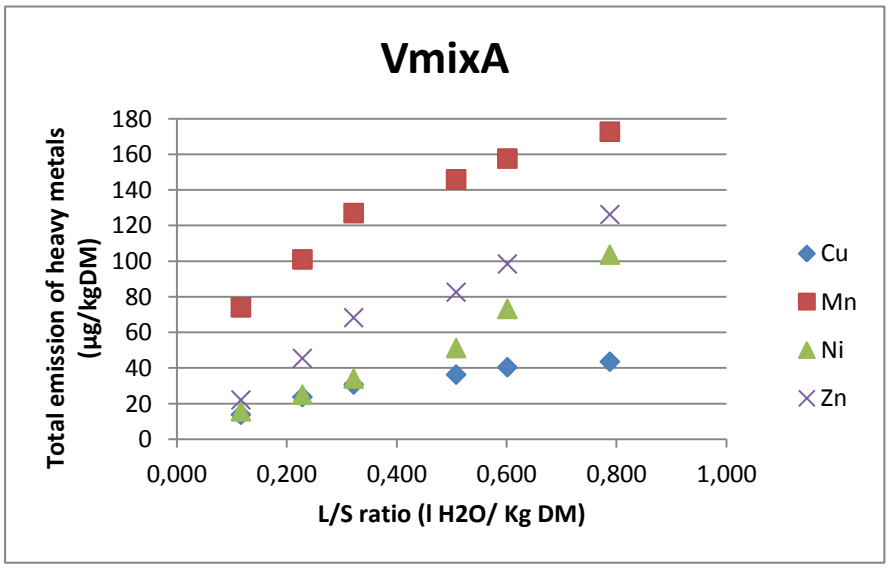


Figure 5-4 - Total emissions of metals from Vmix and VmixB

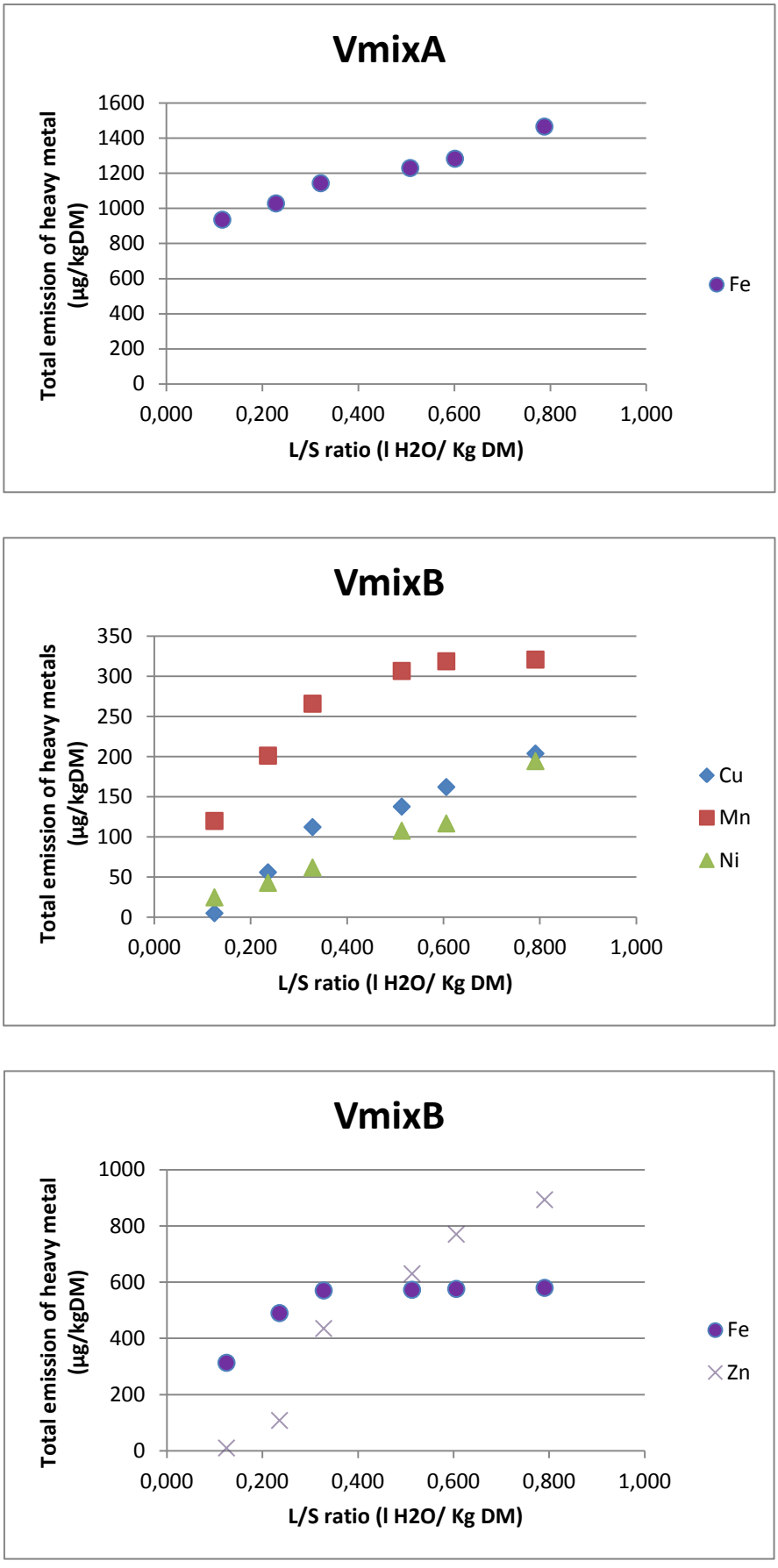
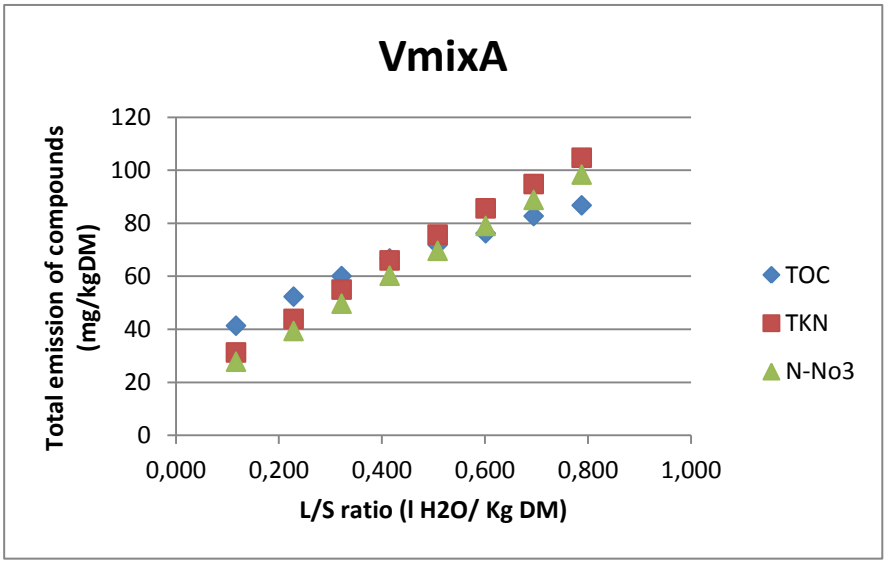


Figure 5-5 - Total emissions of metals from Vmix and VmixB (continuation)



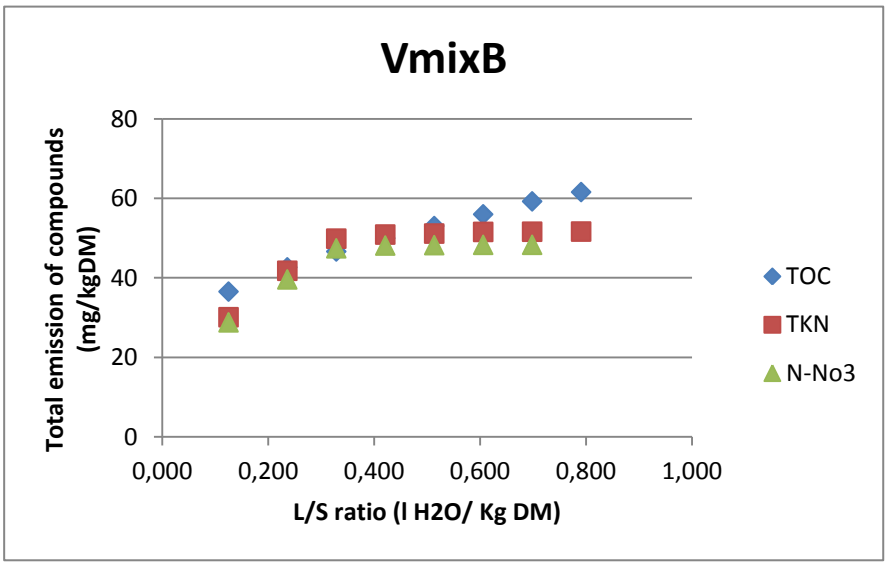


Figure 5-6 - Total emissions of organic fraction from Vmix and VmixB

The leachate presents values that do not exceed the legal limits (Italy and Portugal) taking into account L/S ratio less than 1 l H_2O/ kg DM. The total emissions for the compounds were low for the L/S ratio correspondent. As well as the concentration values of the compounds, the total amounts of emissions are very low, on the order of µg/l for heavy metals. The total emission values of organic fraction did not exceed 120 mg/l.

These results are consistent with the work of Öman *et al*. (2008) for the heavy metals. Öman *et al*. (2008) reported low leachate concentrations most often found for heavy metals, g/l levels, due to immobilization though sorption and precipitation.

For organic fraction, it is noted that the maximum value given in the organic fraction leached from the anaerobic bioreactor (VmixA) does not exceed 110mg/l; leached from the aerobic bioreactor (VmixB), the maximum value is only slightly higher than 60 mg/l.

The values of TOC, TKN and NO_3 were low being among the values for uncontrolled landfills with a high degree of ripeness, which is, closed for over ten years. For a closed uncontrolled landfill, no more than ten years, TOC values are between 100-500 mg/l and NO_3 between 5-10 mg/l (Tchobanoglous and Kreith, 2002). The low values of organic matter dissolved in the leachate, besides dilution, are caused by sorption and degradation (Christensen *et al*., 2001). On the other hand, it is seen that to the reactor under aerobic conditions, had lower TOC, TKN and NO_3 values in the leachate samples.

However, was not possible to establish the maximum value of total emission which this value stabilizes from a particular value of L/S ratio, although the values tend to stability, as expected by the study Fellner *et al*. (2009).

6 Conclusion and future works

Through the study on laboratory scale was possible to check which potential emissions to the level of leachates of uncontrolled landfills. The leachates were compared and were possible to say which ones have more heavy metals and organic fraction emissions.

The main goals of the thesis highlight were:

1. Study of the leachate potential pollution (main emissions) of two uncontrolled landfills, with focus on heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn, As and Hg) and organic fraction (TOC, TKN and NO_3);
2. Compare the compounds levels in the leachate from simulated aerobic and anaerobic bioreactors;
3. Determine the remaining potential pollution using a liquid to solid ratio (L/S ratio).

The reactors were operated in the laboratory with cuisines waste two uncontrolled landfills of waste. Different mixes of the waste samples were operated under aerobic and anaerobic conditions. The leachates were characterized in terms of pH, heavy metals (Cu, Fe, Mn, Ni, Zn) such as and organic fraction (TOC, TKN and NO_3).

Thus, with the work it was concluded that pH is one of the most important parameters to analyse the heavy metals concentration in landfills leachate.

The high pH values presented in the bioreactor results in a low heavy metals concentration in leachate samples. This occurred because high pH values create an optimal environment for sorption and precipitation. The organic matter and soils have significant sorptive capacity at high pH values as well.

On the other hand, the low concentrations of heavy metals may be due to a lack of washing waste in the bioreactor, in other words, a low contact time water/waste.

Through the relation of total emissions and L/S ratio was verified that the "Noè-Tebaldi" landfill has a higher potential pollution than "Servizi Costieri S.r.l" landfill.

In general, the leachates from bioreactors in aerobic conditions presented higher concentrations than the ones from anaerobic conditions bioreactors. The same happened with the leachate quality. The aerobic bioreactors presented leachates with presents values that do not exceed the legal limits (Italy and Portugal) than the anaerobic bioreactors.

The low values of organic matter dissolved in the leachate, besides dilution, are caused by sorption and degradation. On the other hand, it is seen that to the reactor under aerobic conditions, have lower TOC, TKN and NO_3 values of leachate samples. It can be concluded that uncontrolled landfills in which air was injected, the compounds with pollution potential is released in smaller quantities.

The values obtained allow to conclude that both landfills reached their degree of maturation, namely, they are old landfills that biological processes are less active. The maximum contamination has already occurred and the maximum emission of various pollutants stabilized.

For these landfills do not have such a polluting effect throughout his life and after closure, two alternatives could have been used: 1. recovery of waste deposited for use as fuel derived from waste and 2. a conforming closure of the uncontrolled landfill, as described in section 2.2 of this dissertation.

This work was made in a short period of time, taking as a benchmark authors Christensen (2001), Bilgili (2007) and Fellner (2009). This work should be continued in order to improve the adequacy of conditions to vary, including the pH, aeration conditions of contact time and water/waste when washing waste in bioreactors. The work should be continued for a better description of the pollution potential of leachate from landfills in the study.

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